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# CHEMICAL SOLVOLYSIS AS AN APPROACH TO RECYCLE FIBRE REINFORCED THERMOSET POLYMER COMPOSITES AND CLOSE THE END-OF THE LIFE CYCLE

**BY**
**HÜLYA UCAR SOKOLI**

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AALBORG UNIVERSITY
DENMARK

# Chemical Solvolysis as an Approach to Recycle Fibre Reinforced Thermoset Polymer Composites and Close the End-of the Life Cycle

Ph.D. Thesis

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# Abstract

Fibre reinforced polymer composites are engineered materials with superior properties compared to conventional materials such as metals. Therefore, the application of such materials has increased over the last decades and still continues to increase. The major application sectors include aerospace, transport, sports and construction. Although these materials possess great advantages, they are linked to great environmental and societal concerns as they cannot be easily recycled. This can be attributed to the polymer used (thermosets) which have a cross-bond chemical structure, making re-melting and re-molding impossible.

Currently, most fibre reinforced polymer composite waste is landfilled, which is not a sustainable solution. This thesis has studied the use of chemical solvolysis to break down the polymer matrix to either monomers or as energy, and recover the fibres for re-use in new materials.

The use of chemical recycling as disposal route has been investigated the last 15 years. However, overall the technology is still on scientific level as there are still important issues that need to be developed more efficiently. Disregarding the problems that need to be faced within logistics (cutting, shredding and transporting the composite waste etc.), there are difficulties in recovering glass fibres with retained mechanical properties compared to the virgin glass fibres. Carbon fibres can be recovered with retained properties and since they are considerably more valuable than glass fibres, most investigations have been conducted on carbon fibre reinforced plastics. Another issue is the energy needed to conduct the high temperature high pressure experiments and the use of large amounts of solvent.

During this study, investigations have been conducted to recover glass and carbon fibres with retained mechanical properties using a 280 mL batch scale reactor. It was found that when using water as solvent, it was possible to recover the carbon fibres with retained mechanical properties. The glass fibres lost more than 50 % of their strength compared to the virgin glass fibres. However, by replacing water with acetone, it was possible to recover glass fibres with nearly retained mechanical properties. The properties of the carbon fibres were not affected by the use of water or acetone. The depolymerizations of the polymer matrix together with recovery of fibres with nearly retained mechanical properties were achieved at temperatures and pressures down to 260 °C and 60 bar. Furthermore, composite mass/solvent volume ratios up to 2.1 g/mL were enough to achieve the results. The achievement of these results at mentioned process parameters has not been accomplished previously in literature, making this research a very useful attribution to the field of composite recycling.

Regarding the energy consumption used for the chemical recycling process, a study was made to develop a method where the polymer matrix can be converted into fuel,

which potentially can be used in the processing of the composite. A 50/50 vol. % acetone/water mix was used as solvent with or without the catalyst KOH. The solvent mixture in the absence of catalyst converted the polymer matrix into a sticky oil. However, in the presence of catalyst, products produced via. acetone aldol reactions were predominant and represented a large proportion of the oil phase. The oil yield increased 85 % at 325 °C compared to the oil yield obtained in the absence of catalyst. Furthermore, the higher heating value of the oil was nearly 40 MJ/kg and had similar chemical and physical properties compared with crude-oil. An additional advantage of the oil produced from the acetone aldol reactions is that the product was very easy to handle and did not stick to glassware etc. Based on the amount and higher heating value of the produced oil, an estimated calculation showed that the oil in the form of potential chemical energy could provide more than sufficient energy to make an up-scaled process economical sustainable. The excess oil could potentially be used as fuel in other processes.

The overall conclusion from this thesis is that chemical recycling could be a viable solution to recycle fibre reinforced polymer composites, particularly with the results achieved from this Ph.D. study. However, it is suggested that a combination of different recycling technologies will be more efficient to solve the waste problem worldwide.

# Synopsis

Fibre forstærkede polymer kompositter er syntetisk fremstillede materialer med overlegne egenskaber sammenlignet med konventionelle materialer, såsom metaller. Anvendelsen af disse materialer i forskellige industrier er steget meget de seneste årtier og fortsætter stadig med at stige hvert år. De primære anvendelsesområder omfatter rumfart, transport, sport og konstruktion. På trods af det store potentiale samt fordelene ved disse komposit materialer, er de forbundet med store miljømæssige og samfundsmæssige problemer, fordi de ikke kan genbruges på lige fod med f.eks. plastik-flasker o.l. Dette kan tilskrives den anvendte polymer (hærdeplast), som har en tværbunden kemisk struktur, hvilket gør omsmeltning og støbning til nye materialer umulig.

I dag bliver størstedelen af alt fibre forstærket polymer komposit affald deponeret på lossepladser, hvilket ikke er en bæredygtig løsning. Denne ph.d. afhandling omhandler brugen af kemiske opløsningsprocesser ved høje tryk og temperatur til at nedbryde den del af kompositten der består af resin of additiver til enten dets bestanddele eller energi samt at genudvinde fibrene til genbrug i nye materialer. Brugen af kemiske opløsningsmidler til dette formål er blevet undersøgt i hele verden de sidste 15 år. Dog er teknologien overordnet stadig på forskningsstadie. Dette er primært fordi der stadig er vigtige problemstillinger som kræver udvikling. Ses der bort fra logistiske problemer (nedtagning af vindmølle-vinger, neddeling af store komposit materialer samt transport af disse etc.), er der vanskeligheder med at udvinde glas-fibrene med en bevaret mekanisk styrke sammenlignet med de jomfruelige glas fibre. Carbon fibrene derimod er lettere at udvinde med bevarede mekaniske egenskaber, og da de er langt mere værdifulde end glas-fibrene er de fleste undersøgelser udført baseret på carbon fibre forstærkede kompositter. En anden problemstilling forbundet med kemisk nedbrydning er de høje temperaturer of tryk, som kræver energi samt brugen af store mængder opløsningsmidler.

For at løse disse problemstillinger, blev der udført forsøg med det formål at udvinde både glas-og carbon fibre med bevaret mekanisk styrke. Forsøgene blev udført i en 280 mL batch reaktor. Det viste sig at ved anvendelse af vand som opløsningsmiddel var det muligt at genvinde carbon fibrene med bevaret mekanisk styrke, hvorimod glas fibrene mistede mere end 50 % af deres styrke i forhold til de jomfruelige glas fibre. Men, ved at erstatte vandet med opløsningsmidlet acetone, var det muligt også at genvinde glas fibrene med næsten bevarede mekaniske egenskaber. De mekaniske egenskaber af carbon fibrene var ikke påvirket af brugen af acetone som opløsningsmiddel. Disse resultater blev opnået ved lave temperature, tryk samt lave mængder af opløsningsmiddel. Temperatur og tryk kunne komme helt ned på 260 °C og 60 bar. Forholdet mellem kompositten masse/volumen af opløsningsmiddel var helt oppe på 2.1 g komposit/mL opløsningsmiddel. Både glas og carbon fibre udvundet med så høje mekaniske egenskaber ved de omtalte forhold er aldrig opnået

før i litteraturen. Denne forskning giver dermed et yderst brugbart bidrag til forskningen indenfor genbrug af polymer komposit affald.

For at løse problemstillingen med energiforbruget ved kemisk nedbrydning, blev der lavet en undersøgelse med det formål at omdanne resin-delen af kompositten til et flydende kemisk brændstof, som efterfølgende kan anvendes til at gøre processen selvforsynende. Som opløsningsmiddel blev anvendt en 50/50 vol. % acetone/vand mix med eller uden katalysatoren KOH. I forsøgene hvor katalysatoren ikke blev brugt, blev resin-delen omdannet til en klæbrig olie-lignende masse, som var meget svært at håndtere. Hvis der derimod blev tilsat katalysator til opløsningsmidlet, blev der dannet en lang række produkter via. acetone aldol-reaktioner. Disse produkter udgjorde en stor del af olie-fasen. Olie-udbyttet steg med 85 % ved 325 °C i forhold til olie-udbyttet opnået uden brug af katalysator. Brændværdien af olien var næsten 40 MJ/kg og havde lignende kemiske og fysiske egenskaber som rå-olie. Ud fra mængden samt brændværdien af den producerede olie, viste en estimeret beregning, at olien i form af kemisk energi potentielt kan dække energiforbruget i et op-skaleret anlæg og gøre processen økonomisk bæredygtig. Den overskydende olie kan potentielt anvendes som brændstof i andre processer.

Overordnet kan det ud fra denne afhandling konkluderes, at kemisk nedbrydning af kompositter har potentiale til at blive en bæredygtig løsning til at genbruge fibre forstærket polymer komposit affald, især med de resultater, der er opnået i dette ph.d. arbejde. Løsningen på dette affaldsproblem verden over er dog ikke kun kemisk nedbrydning. En kombination af forskellige recyklings-teknologier vil være mere effektiv.

# Preface

This thesis is submitted in partial fulfilment of the requirements for the Ph.D. degree at the department of Chemical Engineering and Bioscience, Aalborg University, Denmark. The Ph.D. project was carried out in supervision of Professor Erik G. Søgaard from the Section of Chemical Engineering at Aalborg University Esbjerg and deals with the use of a solvolysis technology to recycle problematic polymer composite waste by depolymerizing the polymer matrix and recover the fibres.

In the very beginning of my education as a chemical engineer, one of the Associate Professors who introduced us to the University asked:

*"Who wants a Master's degree?" and* then *"Who wants a Ph.D.?"*

I only raised my hand for the Master's degree. At that time, I would never have imagined that 8 years later I will be sitting here and writing a Ph.D. thesis. Why? Well, to be honest, I've never been the great scientist wanting to delve into a subject. However, during my five years at Aalborg University Esbjerg, I got the chance to work on different projects ranging from bio-oil production to self-cleaning surfaces using titanium dioxide. Professor Erik was my supervisor almost from the beginning and gave me the opportunity to explore and carry out all the ideas I got. I evolved … a lot! Research was the first thing on my mind when I woke up and the last thing on my mind when I went to sleep. The possibility to discover something new dragged me more and more into the world of science. So, when Professor Erik provided me with the opportunity to do a Ph.D., the answer was very easy. I accepted and was grateful.

The thesis is structured as a collection of scientific papers. The first part of the thesis is an introduction describing the background for this project. This includes the extent of how big the waste issue is and hence why this research is important. This section ends with a purpose and goals section describing the goals I set for myself from the beginning of the project.

Chapter 2 describes the technical problems associated with the problematic polymer composite waste. It is essential for the readers to know already from the beginning of the thesis why these materials pose a problem worldwide.

Chapter 3 covers the recycling technologies available today, either in large scale or in laboratory scale. The technology (chemical recycling) used in this project is also described in this chapter, including a summary of the finding in the state of the art article written during the PhD study.

Chapter 4 introduces the three different reactors used to conduct experiments throughout the project.

Chapter 5-8 briefly represents the condensed papers. Chapter 5 concerns the effect of e.g. temperature, solvent, additives etc. on the nature of the produced degradation product from the polymer matrix. The chapters 6-8 is concerned with the specific goals set up in the beginning of the project (cf. Section 1.3) and how the goals were accomplished. One of the goals was to develop a method to recover the monomers from the polymer matrix. Chapter 6 condenses the papers concerned with the recovery of monomers. The first goal concerned the fibres. Chapter 7 deals with fibre recovery and their mechanical properties. The last two goals are concerned with energy. Chapter 8 summarizes the findings concerned with fuel production and a calculation about whether the production of fuel is economic sound.

Sitting here today and writing the last lines of my thesis, I realize that the goals necessary to complete the project with success has been accomplished. New and innovative knowledge has been provided to the scientific world. Knowledge which can contribute to solve some of the polymer composite waste problems we as society are facing.

I sincerely hope that you as readers will find the results and the thesis interesting-enjoy your reading.

Hülya Ucar Sokoli

2016

# Acknowledgements

Writing this Ph.D. has been an amazing journey and can somewhat be compared to a maze, where the beginning of the Ph.D. is the entrance of the maze and the exit is the finally completed thesis. In the beginning, you think you are invincible and can complete the maze without any major complications. However, when you bump your head into the first wall, you start realizing that you might not be as invincible as first anticipated. Depending on the speed you hit the wall (and the hardness of the wall), you can get up again and proceed finding the exit or you might need some help to proceed.

During this project I have bumped my head into several walls. Some of them totally knocked me out for couple of hours, days and even weeks (receiving the first papers after revision). Luckily for me, my supervisor Professor Erik and Associate professor Morten E. Simonsen (Aalborg University Esbjerg, AAUE) helped me to jump over this wall. So thank you very much for that. I sincerely appreciate your help and guidance.

After jumping over the wall and getting back on track, you start to feel a bit invincible again. You start running (beginning on new experiments). Until you suddenly find yourself sinking into quicksand (technical problems with reactors, analyzing equipment etc.). You are struggling to get up and feel physically and mentally exhausted. I would like to sincerely thank the hands getting me up, which includes: Dorte Spangsmark and Linda Madsen (Lab technicians, AAUE) and Associate Professor Rudi P. Nielsen for practical and theoretical guidance (AAUE). Grateful thanks also go to my friend and colleague Kasia Arturi (Ph.D. fellow) for mentally helping me getting up again when the obstacles seemed too difficult.

Obstacles which could not be overcome by hands from AAUE include Jens Henriksen from Force Technology and Justine Beauson from DTU. Thank you for conducting the SEM images and tensile strength measurements of the fibres. Our collaboration has resulted in great contributions to the scientific world.

Finally, I would like to thank my dear husband Gzim Sokoli for always supporting me in everything I do. Even though I some days came home confused, mentally and physically exhausted, depressed, sad etc., he always managed to make me laugh. He was my invisible rope holding me up throughout the maze. My family also deserves the warmest thank you for supporting me the whole time. I love you all.

# Thesis details

**Thesis Title:** Chemical Solvolysis as an Approach to Recycle Fibre Reinforced Thermoset Polymer Composites and Close the End-of the Life Cycle

**Ph.D. student**: Hülya Ucar Sokoli

**Supervisor:** Erik Gydesen Søgaard

The main body of this thesis consists of the following papers:

Paper I: Hülya U. Sokoli, Erik G. Søgaard. Review of near-and supercritical recycling of GFR and CFR thermoset polymer materials to find the most cost effective, environmentally friendly and efficient process parameters: State of the Art. Under revision

Paper II: Hülya U. Sokoli, Morten. E. Simonsen, Erik. G. Søgaard. Towards understanding the breakdown and mechanisms of glass fibre reinforced polyester composites in sub-critical water using some of the most employed and efficient additives from literature. Submitted

Paper III: Hülya U. Sokoli, Justine Beauson, Morten E. Simonsen, Anthony Fraisse, Povl Brøndsted, Erik G. Søgaard. Valorization of polymer composite waste by recovering the glass-and carbon fibres with retained mechanical properties simultaneously with the production of a valuable oil product. Submitted to Journal of Industrial and Engineering Chemistry Research

Paper IV: Hülya U. Sokoli, Morten E. Simonsen, Rudi P. Nielsen, Katarzyna R. Arturi, Erik G. Søgaard. Conversion of the matrix in glass fibre reinforced composites into a high heating value oil and other valuable feedstocks. *Fuel Processing Technology*. 149 (2016) 29–39.

Paper V: Hülya U. Sokoli, Rudi P. Nielsen, Erik G. Søgaard, Morten E. Simonsen. Microwave induced degradation of glass fibre reinforced polyester for fibre and resin recovery. 20$^{th}$ *International Conference on Composite Materials.*

Paper VI: Hülya. U. Sokoli, Erik G. Søgaard. Supercritical Degradation of Unsaturated Polyester Resin Composites Using Alcohols. *Chemical Engineering Transactions*. Vol. 43, 2015.

Paper VII: Hülya U. Sokoli, Morten E. Simonsen, Rudi P. Nielsen, Jens H.H. Henriksen, Niels H. Pedersen, Marianne L. Madsen, Erik G. Søgaard. Characterization of the liquid products from solvolyzed epoxy- and polyester resin based composites using solid-phase microextraction and recovery of the monomer phthalic acid. *Industrial and Engineering Chemistry Research*. 2016. DOI: 10.1021/acs.iecr.6b02111

Paper VIII: Hülya U. Sokoli, Erik G. Søgaard. Recycling Supercritical Acetone-The Effect upon Glass Fibre Reinforced (GFR) Epoxy Resin Degradation. Submitted to ChemSusChem.

In addition to the papers, following oral presentations and poster presentation have also been made.

**Oral Presentations**

Hülya U. Sokoli, Rudi P. Nielsen, Erik G. Søgaard, Morten E. Simonsen. Microwave induced degradation of glass fibre reinforced polyster for fibre and resin recovery. *Presented at 20th International Conference on Composite Materials.* 19-24th July 2015.

Hülya U. Sokoli, Erik G. Søgaard. Closing the life cycle of waste fibre reinforced polymer composites by converting it into valuable products. *2nd World Congress and Expo on Recycling* July 25-27, 2016 Berlin, Germany.

**Poster Presentation**

Hülya U. Sokoli, Erik G. Søgaard.
Degradation of Composites using near-and supercritical fluids. *ICheaP12 International Conference on Chemical and Process Engineering*, Milan, 19-22 May 2015.

This thesis has been submitted for assessment in partial fulfillment of the PhD degree. The thesis is based on the submitted or published scientific papers which are listed above. Parts of the papers are used directly or indirectly in the extended summary of the thesis. As part of the assessment, co-author statements have been made available to the assessment committee and are also available at the Faculty. The thesis is not in its present form acceptable for open publication but only in limited and closed circulation as copyright may not be ensured.

# Table of contents

# 1. Introduction

This thesis is concerned with the chemical recycling of fibre reinforced polymer (FRP) composite waste. Recycling of plastic waste is a hot topic being discussed more than ever all over the World nowadays, particularly after the implementation of several EU Directives aiming at creating more focus on reducing, reusing and recycling plastic waste. A great part of this is due to the landfills bulging with plastic waste, where FRP composite waste represents one of the greatest issues due to the problematic structure of the polymer matrix (cf. Chapter 2). Nevertheless, FRP composite materials have become an important part of our daily life and the use of such materials increase every year, producing more and more waste which has to be handled in an efficient and sustainable manner.

"The combination of two or more different materials to form a new material with enhanced material properties". This is the broad definition of a composite material. The use of composites is well documented in history and goes back to ancient time. Human development and civilization are closely linked to the use of different materials and provide milestones in human progress. In a material point of view, human society has experienced Stone Age, Bronze Age and Iron Age [1]. Early in history, it was well known that by combining different materials, it was possible to produce properties superior to those of the individual components. Ancient Egyptians and Israelite workers incorporated chopped straw in bricks to reinforce the structural integrity [2-3]. Even Homer's Illiad describes Achilles shield made of a composite [2].

The progress of civilization made the requirements to a wide range of materials increasingly severe. This includes the aerospace, automotive and weapon industries etc., as they require materials that are stronger, lighter, cheaper and more resistant to temperature and corrosion. To meet such requirements, advanced high-performance composite materials are undoubtedly the best answer. These materials were introduced in the $20^{th}$ century and can basically be divided into three main types of materials which include:

**Metal matrix composites** (**MMC's**) consist of a metal, such as aluminum, which is reinforced with particulates or fibres of a ceramic material, e.g. continuous carbon, silicon carbide, or ceramic fibres.

**Ceramic matrix composites** (**CMC's**) consists a ceramic matrix reinforced with ceramic fibres. The matrix and fibres can consist of any ceramic material.

**Polymer matrix composites** (**PMC's**) consist of a polymer matrix with fibres as reinforcement. The most used fibres are glass, carbon and aramid fibres.

PMC's are cheaper and easier to manufacture than the other types of composites and because of the inherent characteristics of PMC's, they have become the fastest growing and most widely used composite materials [1]. This can, among many other properties be attributed to the high specific strength and high specific modulus, which relates to the bearing capacity and stiffness properties of the material. Such properties are considerably important for aerospace applications.
Other advantageous properties include lighter weight, higher performance, non-corrosive, good electrical insulating properties and the possibility of production in any shape. This makes PMC's suitable as substitutes for a wide range of existing structures and extends their life [4].
PMC's is named depending on the reinforcement. If the reinforcement is glass fibres, the PMC is called glass fibre reinforced polymer (GFRP) composite and if the reinforcement is carbon fibres, the PMC is called carbon fibre reinforced polymer (CFRP) composite. Both type of fibre reinforcement is widely used today. In fact, according to the Composite Market Report from 2015 [5], the GFRP composite production volume in Europe was estimated to 1069 kilotonnes (Fig. 1, left). The CFRP composite demand was estimated to 91.000 tons globally in 2015 (Fig. 1, right). Therefore, GRP composites continue to be the biggest material group in the composite industry, posing more than 95 % of all FRP composites (short and long fibres, rovings, mats etc.) [5].

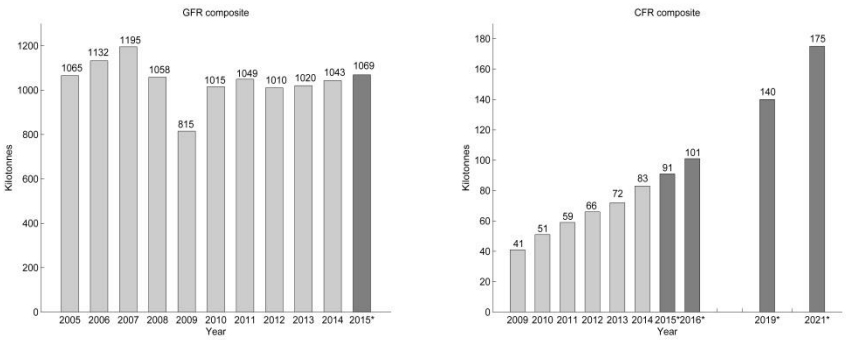


*Fig. 1 Left: Glass fibre reinforced composite production volume in Europe, where 2015 is an estimated value. Right: Carbon fibre reinforced composite demand globally in 1000 tonnes, where 2015-2021 are estimated values (Data values from Composite Market Report 2015[5])*

The share of GFRP application industries is shown in the pie-chart in Fig. 2 (left). A third of the produced GFRP composites are used in the transportation sector, which includes the vehicle industry, locomotives, boats and air crafts. Another third of the production volume is used for the construction industry, which includes wind turbine blades and offshore applications etc. Other areas of applications are electronics, sports and leisure [6]. The share of the CFRP application industries are also shown in Fig. 2 (right). The major application industry is aerospace with 31 % of the share.

The second largest application area is automotive, followed by wind turbines and sports. The GFRP composite industry is predicted to grow at a rate of 2.5 % yearly, and the CFRP composite industry is predicted to grow at a rate of 10.6 % yearly [5].

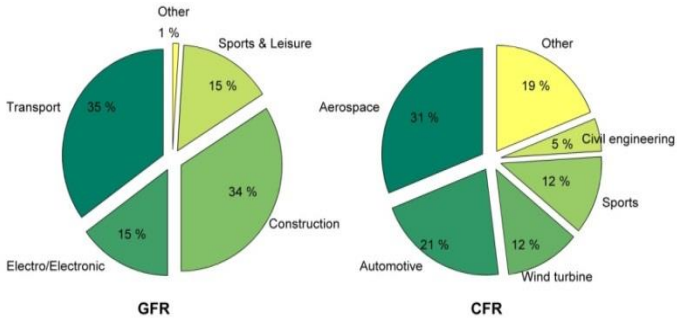


*Fig. 2 Left: Breakdown of GFR by application in Europe 2014. Right: Breakdown of CFR composites by application globally in 2015. (Data values from Composite Market Report 2015[5])*

Despite the increasing utilization of PMC's and the great advantages of the materials, the disadvantages might be just as high due to the serious issues related to recycling them. This generates large amounts of production scrap and End-of-Life waste from the materials. For example, wind turbines have a life-time of approx. 20-25 years [7]. After the life time, approx. 94 % of the turbine can be recycled, where the recyclable materials includes steel, aluminium and a smaller amount of copper. The 6 % which is not recyclable includes the fibre reinforced polymer (FRP) composite materials, namely the blades [8]. According to estimations by Albers et al. [9], every kW wind power requires approx.10 kg blade material. This will produce nearly 50.000 tonnes of waste from wind turbine blades in 2020, rising to more than 200.000 tonnes in 2034 worldwide [9]. These numbers are only from the wind industry. Even larger amounts of FRP composite waste is generated by the other industries, cf. Fig. 2, indicating that the society will face major issues in the upcoming years concerning these materials.

## 1.2 The need to recycle

The majority of FRP composite waste generated worldwide is still landfilled [10-11]. This can mainly be attributed to the fact that landfilling is the easiest and cheapest disposal route [12]. However, landfilling is not a sustainable disposal route in the long term. Concern for the environment has led to increasing pressure to recycle FRP composites at the End-of-Life and production scrap from the industries. Therefore, waste management has over the last years been of high priority within the European Union, resulting in the implementation of the Waste Framework Directive (2008/98/EC). This Directive sets the basic concepts and definitions related to waste management, cf. Fig. 3.

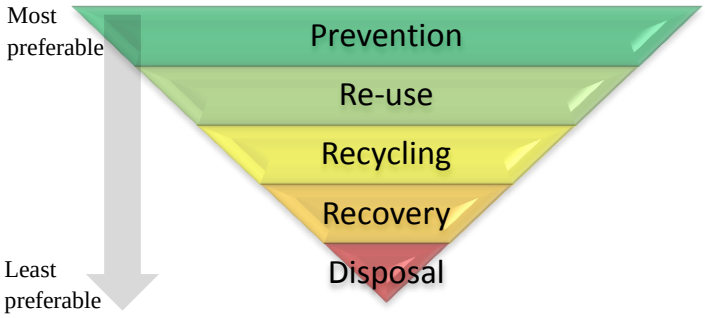


*Fig. 3 Waste management hierarchy*

Preventing the waste is the most preferable solution and includes using less material in the design or develop a material with similar properties but more easily recyclable. In fact, a new project (DreamWind) initiated in Denmark (2016) with focus on developing alternative materials to PMC's for wind turbine blades that can be easily recycled again [13]. However, if a new, more sustainable material is developed, several years will pass before the new materials will be implemented and used in the wind turbine industry. Thus, a great amount of FRP waste still has to be handled today and in the up-coming years.

The second preferred waste management route is reuse, meaning that the FRP's are used again in another material. For example, LM Windpower sells some of their wind turbine blades to other countries after they have reached their End-of-Life. Additionally, a Dutch architectural firm (2012Architecten) reused discharged wind turbine blades to create an interactive playground in 2008 [14]. Although the FRP waste can be reused efficiently, the materials will eventually have to be handled again either by recycling, recovery or disposal.

Recycling involves turning the FRP waste into new materials or products. This includes recovering the fibres and reusing them in new composite materials or recovering the monomers in the polymer matrix and reuses them in new polymeric materials. Recovery also involves incineration of the FRP waste resulting in energy recovery, or pyrolysis which produces fuel oil. The least preferable disposal route is landfilling and incineration without any energy recovery.

In addition to the Waste Framework Directive (2008/98/EC), several other Directives affecting the FRP industry includes; The Landfill Directive amended in 1999 (99/31/EC), the Incineration of Waste Directive in 2000 (2000/76/EC) and the End of Life Vehicles Directive in 2000 (2000/53/EC). These directives resulted in stricter regulations in several EU countries, putting more pressure on producers to consider waste treatment. In fact, Sweden and Germany has prohibited landfilling of composite waste [6].

Therefore, handling FRP waste is crucial. Research and development of technologies to recycle FRP composites has been ongoing for approx. 35 years [6]. Among the major initiative for finding sustainable recycling technologies in Denmark, GenVind (Reuse) initiated in 2013. This Ph.D. project has been a part of this project.

## 1.3 Purpose and goals

The purpose of this work is to use chemical degradation as the technology for recycling FRP composites. Several goals were established from the beginning of the project, in order to develop a sustainable, economic and environmental sound technology (cf. Fig. 4).

This included: 1) Developing a method which can recover both glass-and carbon fibres with retained or nearly retained mechanical properties, 2) Recovery of monomers which potentially can be used in new polymers, 3) Recovery of energy to make the process energetically viable and 4) to achieve all the goals using minimum energy and solvent consumption.

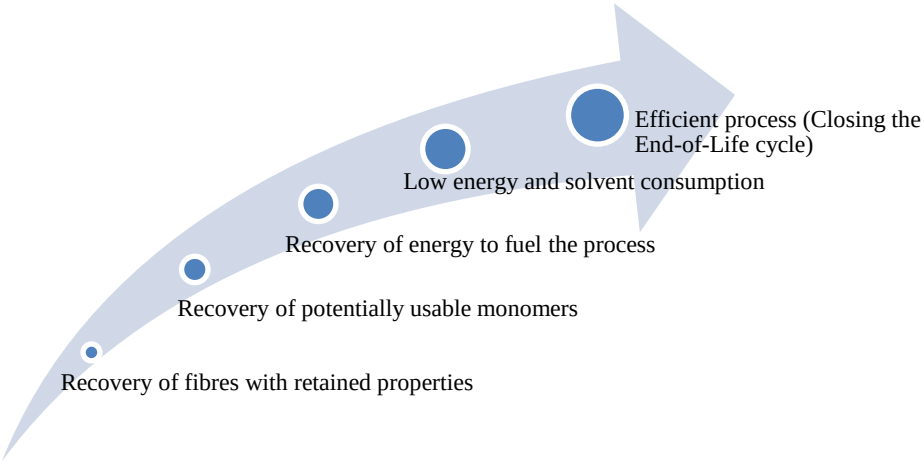


*Fig. 4 Goals set up for this PhD project, in order to efficiently close the loop on the End-of-Life cycle for fibre reinforced polymer composites.*

Fulfilling the goals set up for this project, following approaches were used:

- The use of 280 mL and up-scaled to 1 L high pressure batch reactors to conduct the experiments at temperatures ranging at 200-350 °C and pressures ranging at 50-300 bar.
- The use of single fibre tests to study the mechanical properties of the recovered fibres
- The use of GC-MS and SPME-GC-MS to discover the nature of the degradation products, in order to follow the polymer degradation pathways and hence attain knowledge about process conditions at which monomers are released from the polymer.
- Calorific value measurements of the solubilized resin after being subjected to the chemical solvolysis process, to gain knowledge about the energy content.

# 2. FRP composite recycling difficulties

To describe the technical problems related to the recycling of FRP composites, it is essential to gain knowledge about polymer composites, including their structure and constituents.

## 2.1 FRP composite structure

A composite is a material made from two or more constituent materials with different physical or chemical properties. The two (or more) materials remain separate and distinct within the finished structure; cf. Fig 5 for the structure of a FRP composite. The fibres or the polymer matrix are not well suited for construction purposes on their own, but in combination, they results in a rigid material with superior properties, such as high strength to weight ratio, none-corrosive and easy to construct [15]. The fibres provide strength, stiffness and thermal stability to the composite and the polymer matrix bind the fibres together, protect and transfer load between them. The major issue in terms of recycling these materials can be found in the polymer matrix holding the fibres together.

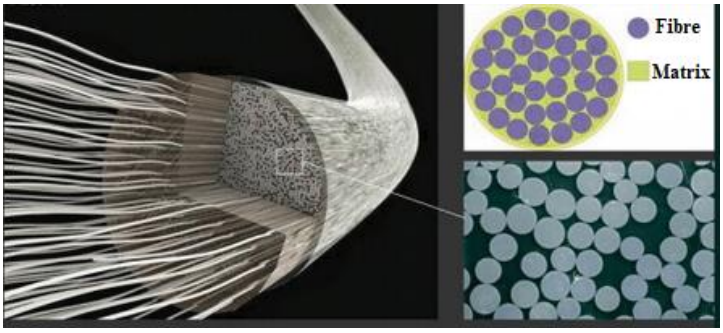


*Fig. 5 Cross-section of a fibre reinforced polymer composite [16]*

## 2.2 Polymer matrix

A polymer is defined as a macromolecule with very high molecular weight, which is comprised of smaller repetitive molecular units (monomers) [17]. The geometry of a polymer can be linear, branched or have a crosslinked network structure, which strongly influences the properties of the given polymer. Linear polymers (Fig. 6) are commonly called thermoplastics. The monomer molecules within the polymer chains are bond to each other through strong covalent interactions, whereas the monomers between the polymer chains bond to each other through weak Van der

Waal intermolecular forces. The weak bonds can be broken by heat, why thermoplastics typically have easily accessible melting points. The melted thermoplastic can then be re-processed into new desired shapes. Once the thermoplastic has cooled, the weak Van der Waals bonds in between the monomer chains will form reversibly, making the new material rigid and usable again.

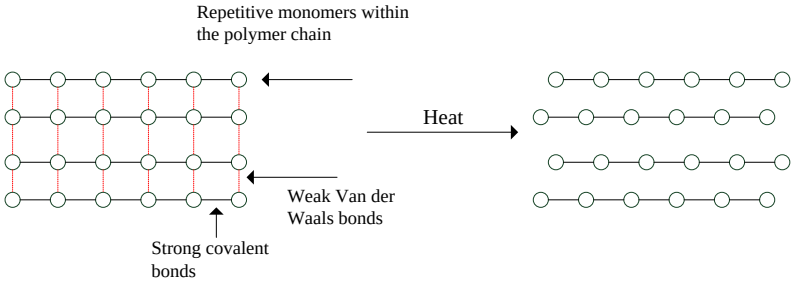


*Fig. 6 Geometry of thermoplastics before and after being subjected to heat*

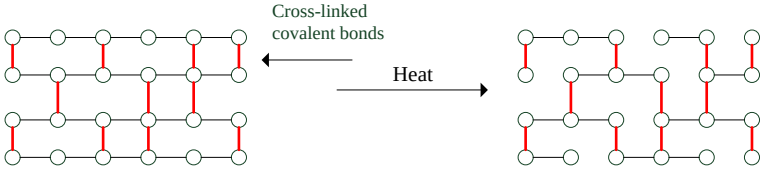


*Fig. 7 Geometry of thermosetting plastics before and after being subjected to heat*

Therefore, these types of plastics are readily recycled. Examples of thermoplastics includes; Nylon, polycarbonate, acrylonitrile, polypropylene, polystyrene, teflon, polyvinyl chloride etc. [18]. The materials are often used in commodity, such as film for packaging, clothing, beverage and trash containers and a variety of household products.

Compared to thermoplastics, the properties of thermosetting plastics (Fig. 7) are superior in terms of thermal stability, high rigidity, high dimensional stability, chemical resistance, resistant to creep or deformation, high electrical and thermal insulation properties etc. These properties can be explained by the three-dimensional cross-linked geometry of the polymer, cf. Fig. 7. The cross-linked bonds between the polymer chains are strong covalent bonds, unlike the weak Van der Waals bonds in thermoplastics. On exceeding the decomposition temperature, the thermoset polymer will be chemically decomposed [18]. Therefore, these materials cannot be reshaped or recycled upon heating. Examples of thermoplastics includes: Epoxy resin,

unsaturated polyester (UP) resin and phenolic resin. Due to the superior properties of thermosets, they are often used in applications with demanding requirements; for example as the polymer matrix in fibre reinforced composites. Since epoxy and UP resins are among the most used thermoset plastics worldwide [19] and the polymer matrix of the composites used for the investigations during this PhD study, the manufacturing of these thermoset polymers will be described more detailed.

### 2.2.1 Epoxy resin

Epoxy resin covers a broad class of thermosetting plastics in which the primary cross-linking occurs through the reaction of an epoxide group, cf. Fig. 8. Therefore, an epoxy resin is defined as a molecule with more than one epoxy group. The molecular base to which the epoxy group is attached can vary widely, yielding various classes of epoxy resins, which can be tailored to fit a broad range of applications.

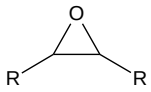


*Fig. 8 Basic chemical structure of epoxy group*

One of the most important raw materials used for the production of epoxy resin is epichlorhydrin, which is used as a precursor for almost all commercially available epoxy resins [20]. Condensation reactions between epichlorhydrin and bisphenol A produces the first commercial epoxy resin, namely diglycidyl ether of bisphenol A (DGEBA), which is still one of the most employed epoxies today, cf. Fig. 9. Other commonly used epoxies include phenol novolac, bisphenol A novolac, triglycidyl p-aminophenol, dicyclopentadiene novolac, tetraglycidyl methylene dianiline (TGMDA) etc. [20]. The latter is used extensively for aerospace applications due to the high temperature stability and excellent mechanical properties.

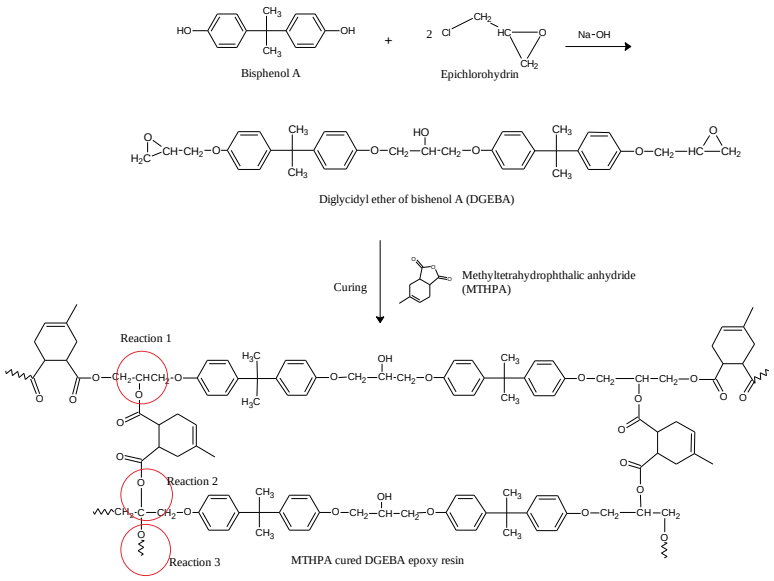


*Fig. 9 Curing of DGEBA epoxy resin with MTHPA*

### 2.2.2 Epoxy resin hardeners

Conversion of the epoxy resin to epoxy plastic requires a curing agent or also called a hardener. The most common types of hardeners for epoxy resin include amines, amine derivatives and acid anhydrides [21]. The curing process can take place at temperatures in the range of 5 to 260 °C, depending on the hardener. In general, epoxy resin can be cured with amines or amides at room temperature, whereas acid anhydrides often require higher temperatures to react with the epoxy resin. DGEBA epoxy resin cured with acid anhydride has been used for the studies in this thesis. An example of the curing between DGEBA epoxy resins with acid anhydrides such as methyltetrahydrophthalic anhydride (MTHPA) is shown in Fig. 9.
In general, the reaction between an acid anhydride and epoxy resin is complex, as three competing reactions takes place. The anhydride reacts with the epoxy hydroxyls (reaction I) forming an ester bond. The free carboxyl group on the MTHPA curing agent is then available to react with an epoxide ring (reaction II), generating another hydroxyl. This hydroxyl group can again react with another anhydride (reaction 3). The benefits of using anhydrides as curing agent is the longer lifetime of the epoxy plastic and the low potential for skin irritation [20].

### 2.2.3 Unsaturated polyester resin

Unsaturated polyester (UP) resins are the most commonly used thermoset resins today. The resin is used for a wide range of applications, such as for pipes, tanks, high performance components, marine and in the automotive industry. UP resins are prepared by condensation polymerization of unsaturated di-carboxylic acids and diols [22]. The unsaturation provides a site for cross-linking with a vinyl reactive monomer, most commonly styrene. Peroxides are often used as free radical initiators for the curing process. The relative proportions of acids, diols and styrene vary depending on the desired properties of the final UP plastics. UP resins can be classified into categories depending on the dicarboxylic acid used.

**Ortho-phthalic polyester** resins are made from ortho phthalic anhydride and generally cheaper than the two other classes of UP resin. This type of UP resin is used to manufacture general purpose composite laminates where only moderate structural properties are required (shower stalls, boats, swimming pool, water tanks etc.).

**Iso-phthalic polyester** resins are made from iso phthalic anhydride and more structurally competent compared to ortho phthalic resins. Together with the superior corrosion resistance, these types of UP resins are used for more demanding applications.

**Tere-phthalic polyester** resins are made form tere-phthalic acid and currently used in small volumes, as it is considered as a specialty resin. This type of resin tends to have better thermal and chemical resistance than iso-pthhalic acids, but more difficult to manufacture [23].

General purpose UP plastics are prepared by maleic anhydride, phthalic anhydride and propylene glycol with molar ratios of phthalic anhydride:maleic anhydride ranging from 1:2 to 2:1. Styrene is used for cross-linking and small amounts of peroxide as initiator [22]. Similar monomers were also used for the polymer composites used in the investigations during this thesis. A proposed structure of the cured UP resin is shown in Fig. 10.

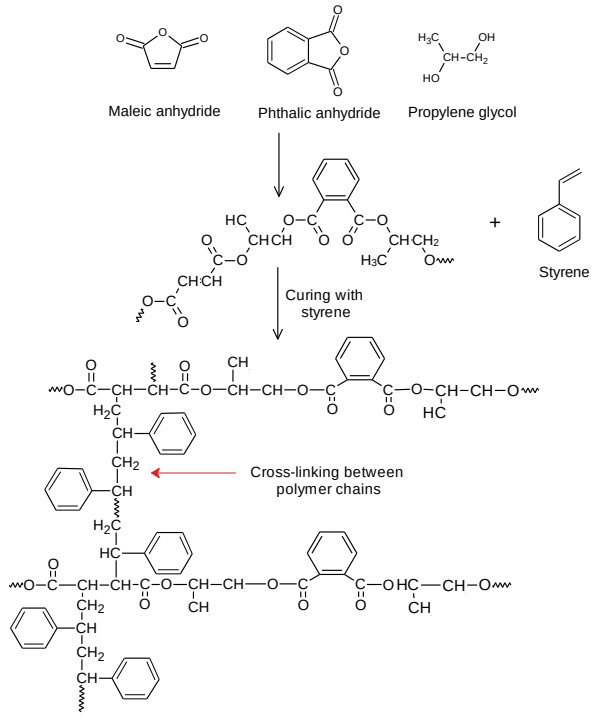


*Fig. 10 Cross-linking of UP resin by styrene*

# 3. Recycling Technologies- State of the art

Since the beginning of the 1980's, great efforts have been made to develop potential recycling technologies for FRP composite waste. These technologies can be divided into three main categories as shown in Fig. 11. The following sections will provide an introduction to each recycling technology and briefly summarize the state of the art in each field, including the benefits and drawbacks of each technology.

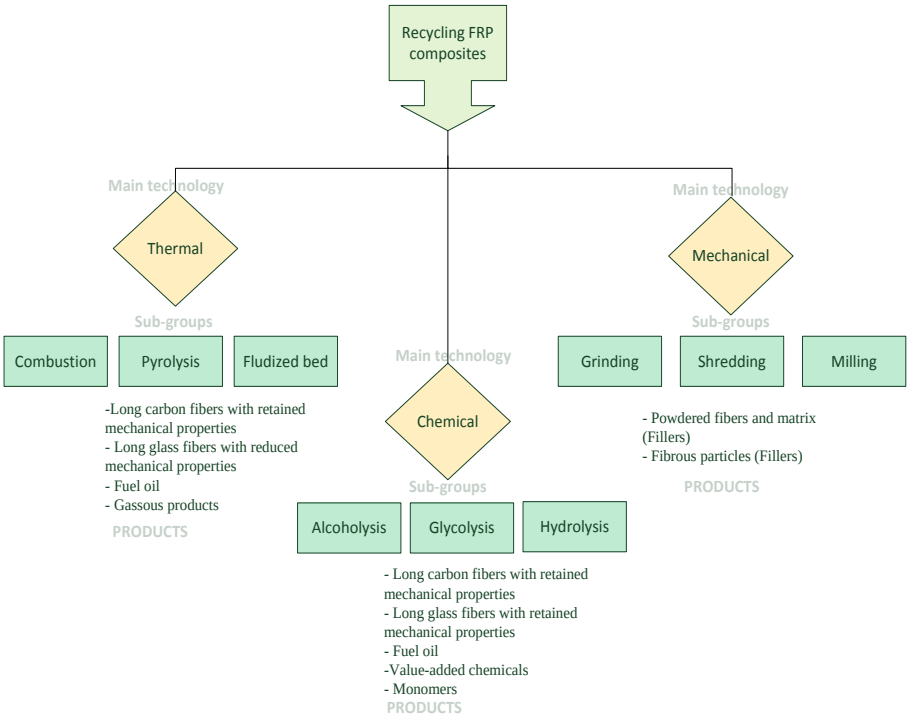


*Fig. 11 Main recycling technologies and their subgroups.*

## 3.1 Mechanical recycling

Mechanical recycling is used to break-down the FRP composites mechanically by shredding, crushing, milling, grinding and the similar. This produces composite fragments of different sizes which can then be separated into powdered products (rich in resin) and fibrous products (rich in fibres) [24]. The powdered products can be used as fillers and reinforcement in new composites or other applications. Recovery of individual fibres is not possible using this recycling route. Most

research within mechanical recycling of FRP composites has been focused on the recovery of GFR composites, as the products present low-value applications [25].

Demonstration or commercial scale plants that are and has been implemented around the world is shown in Table 1. In general, it has been proven that mechanical recycling on industrial scale is feasible. However, the value of the end-products is reduced to that of calcium carbonate, which can be purchased at very low cost (150-200 $/tonne). In addition, considerable amounts of energy are required to grind the composites to powder/small particles [26]. The utilization of the technology is therefore uneconomical, resulting in low levels of use and imbalance between the collectable waste and the potential market for recyclate [27]. Thus, attempts to commercialize mechanical grinding as a recycling route have failed.

*Table 1. Demonstration-scale plants implemented worldwide.*

| Recycling company | Country and year | Process scale | Products |
|---|---|---|---|
| European Composite Recycling Technology A/S [28] | Denmark (2012) | N/A | -Powders<br>-Fibres (1-10 mm) |
| ERCOM [29] | Germany (1992-2004) | N/A | -Powders<br>-Fibres |
| Mixt Composites Recyclables (MCR) [30] | France | N/A | -Powders<br>-Fibres |
| ECO-wolf Inc. [31] | USA (2011) | N/A | -Fibres (3-25 mm) |

### 3.1.1 Summary

Mechanical recycling can recover both the fibres and the resin without any use of chemical solvents or hazardous materials. However, the fibres are small, unstructured, coarse and non-consistent [32]. Furthermore, it is not possible to recover long fibres using this technology, limiting the possibilities for their re-manufacturing.

## 3.2 Thermal recycling

Thermal recycling involves the use of heat to depolymerize the polymer matrix and recover the fibres. The technology can be sectioned into three further categories, which includes combustion, pyrolysis and fluidized bed.

### 3.2.1 Combustion

The polymer matrix of FRP composites can be combusted at temperatures in excess of 850 °C with the main purpose of recovering energy and converting it into electricity [33]. Thermoset polymers, such as epoxy and polyester have calorific values around 30 MJ/kg [24]. However, when reinforced with fibres in varying ratios, the calorific value decreases down to 6-7 MJ/kg [34], meaning that the energy recovery per kg waste is lowered considerably. In fact, it has been reported that the incineration of composite materials for energy recovery results in energy loss in the region of -400 kJ/kg [27]. Additionally, large quantities of inorganic residue, such as glass fibres, fillers and ash will be left after the combustion process. This residue requires disposal, e.g. by landfilling, which reduces the sustainability of the method and making this recycling approach less efficient.
However, when the combustion process is carried out in a cement kiln, the sustainability of the combustion process can be improved slightly by using the glass fibres in the cement and the polymer matrix as a source of heat. The heat from the polymer reduces the overall costs of cement production, particularly because heat is the major cost in cement production. Important requirements for this process are that the composite specimens must be of a designated size, not contain toxic materials and heavy metals and have a specific calorific value [27, 34]. Furthermore, the cement industry charges a fee for recycling the composite waste (estimated to 1 euro per kg waste) [27].

### 3.2.2 Fluidized bed

The fluidized bed process involves the use of a silica sand bed that is thermally heated and fluidized by hot air at elevated temperatures (450-550 °C). Prior to fluidizing the silica sand, the FRP composites are fed into the bed of silica sand. The polymer matrix is then vaporized by the hot air and used to produce heat and energy. The fibres and the silica particles are transported out from the bed in the hot air stream. The recovered fibres are finally separated from other solid particles in a cyclone [25, 35]. Carbon fibres can be recovered with only 20 % reduction in tensile strength compared to the virgin carbon fibres after processing at 550 °C [34]. Glass fibres are more susceptible towards the harsh environments in the fluidized bed, why the tensile strengths are lowered considerably compared to the virgin glass fibres. Pickering et al. [36] recovered glass fibres by means of the fluidized bed process at different temperatures. They found that the glass fibres lost 50 % of the tensile strength at 450 °C and 90 % at 650 °C. No demonstration-scale plants have been implemented so far using this technology.

### 3.2.3 Pyrolysis

Pyrolysis of FRP composites involves heating to 450-700 °C in the absence of oxygen and in an inert atmosphere (e.g. nitrogen). The polymer matrix is converted

into gaseous products (e.g. $CO_2$, $H_2$, $CH_4$ and other hydrocarbons) and a liquid product (tar and other heavy liquids) [35]. The calorific values of the gaseous and liquid products vary depending on the polymer matrix and pyrolysis process. A sheet moulding composite (SMC) of polyester converted into gas- and liquid products exhibited calorific values of 19 MJ/kg for the gas and 37 MJ/kg for the liquid fuel [24].
The carbon fibres can be recovered with nearly retained mechanical properties (4-20 % loss in tensile strength) [25], whereas the glass fibres are more susceptible towards the high temperatures and loose more strength, up to 80 % - 84 % [37-38]. Due to the considerably higher value of carbon fibres and their stability at high temperatures, nearly all demonstration or commercial -scale plants that is and have been implemented worldwide has been on CF recovery, cf. Table 2. Recovery of CF products provides materials with considerably higher value than end-product from recovered glass fibres (fillers), why some of the recycling companies are growing industries. The recycling company ELG carbon fibre claims to be a leading global CF plastic recycler. They have implemented a commissioned full scale industrial recycling plant and produce a range of products from recovered CF's. The company has capacity to process in excess of 2000 tonnes of CFR composite waste per year [39]. Other pyrolysis large-scale recycling plants are situated in Japan, USA, Italy, Denmark and Germany.

The recycling company ReFiber in Denmark produced insolation mats and balls from recovered glass fibres. However, the company went bankrupt in 2007 due lack of recycling materials. According to Erik Grove-Nielsen from ReFiber, the fibre recycling market has to be more secure before getting into it. There has to be a "cry" for the service [26]. In other words, the composite industries in Denmark have to be forced, through legislation, to recycle their waste instead of the opportunity to landfill.

Table 2. Demonstration and commercial-scale plants implemented worldwide

| Recycling company | Country and year | Process scale | Products |
|---|---|---|---|
| ELG carbon fibre Ltd. [39] | UK (2009) | >2000 t/year | -Milled CF's<br>-Chopped CF's<br>-Pelletized CF's<br>- Reconstituted CF yarn<br>-Discontinuous chopped CF's |
| The Japan Carbon Fibres Manufacturers Association (JCMA)[1] [40] | Japan (2006) | 1000 t/year | Targeted for consumer electronics and automotive industries. |
| Carbon Conversions [41] | USA (2010) | 2300 t/year | -Raw chopped CF's<br>- CF's in rolls |
| Karborek [42-43] | Italy (1999) | 1500 t/year (planned) | -Chopped CF's<br>- Felt mat<br>Milled CF's |
| ReFiber[2] [44] | Denmark (2002) | 5000 tons/year (planned) | -Insulation Wool Mat from GF's<br>-Insulation GF balls<br>-Chopped CF's |
| CFK Valley Stade Recycling [45] | Germany (2010) | 1000 tons/year | -Milled CF's<br>-Chopped CF's<br>-Textile products |
| HADEG Recycling Ltd.[46] | Germany (1995) | N/A | -Short CF's<br>-CF yarns<br>-Unidirectional warp cloths<br>-Multi-axial warp cloths |

[1]Merged into Japan chemical Fibres Association (JCFA) in 2014
[2] Went bankrupt in 2007

### 3.2.4 Summary

The advantages of the thermal processes are that no chemical solvents are used and that the products can be recovered and reused in one form or another. The resin can be reused as energy required for the process. The fibres (in varying sizes) can be reused as reinforcement, similarly as the fibrous fractions produced from the mechanical recycling processes. Furthermore, the carbon fibres can be re-manufactured into new composite materials, since the mechanical properties are nearly retained. However, recovery of glass fibres with retained mechanical properties has not been possible using this technology, why the technology is restricted to recycle CFRP composites, unless high glass fibre strengths are not necessary for the end product. Furthermore, recovery of monomers is also difficult due to the high temperatures, which decomposes the monomers into smaller degradation products.

## 3.3 Chemical recycling (solvolysis)

Chemical recycling, also called solvolysis, is a technology where a solvent, (e.g. alcohols, water, glycols, ketones) and catalysts/additives are used to depolymerize the thermoset polymer matrix by breaking down the cross-linked chemical bonds. The polymer can either be subjected to total depolymerization back to its monomers or partial depolymerization into oligomers and other industrial chemicals [47].

Solvolysis can be sectioned into two categories:

**Low temperature solvolysis:** Below near- and supercritical temperature and pressure, often carried out at atmospheric pressure.

**Near- and supercritical temperature solvolysis**: In- and above near- and supercritical temperature and pressure.

Investigations have been conducted within both categories during this PhD study. The investigations conducted within the literature are summarized in a review paper (paper I). The following sections will briefly introduce the most important findings within low temperature solvolysis and near-and supercritical temperature solvolysis.

### 3.3.1 Low temperature solvolysis

Low temperature solvolysis is conducted with reactive solvents such as nitric acid, sulfuric acid, ammonia and glycols. This technology was among the first investigations made towards chemical degradation of FRP composites and has been investigated by several authors, cf. Paper I for details.

Nitric acid with concentrations of 8 M and 12 M at 90 °C has been used to degrade CFRP composites within 12 and 6 h, respectively [48-49]. The carbon fibres where recovered with nearly no loss in mechanical properties. Sulphuric acid (unknown concentration) in the presence of hydrogen peroxide ($H_2O_2$) has also been used for CFRP recycling. The authors emphasized the importance of stirring during the depolymerization process, as nearly no degradation was achieved without stirring [50]. Organic solvents, such as benzyl alcohol in the presence of tripostassium phosphate have also been used to recover carbon fibres. The depolymerization time was within 5-20 h, depending on the thickness of the composites. The investigations were conducted at 200 °C under ambient pressure [51].

**Summary**

Low temperature solvolysis is efficient for depolymerizing thermoset polymers and recovers the fibres with nearly retained mechanical properties. The benefit of this technology is that the degradation process can be conducted without pressure. High

pressures require more expensive reactor components capable of withstanding the high pressures, such as valves and pipes. Another benefit is that low temperatures are used, reducing costs related to energy requirements.

The drawbacks are the long reaction times and the aggressive, corrosive and sometimes environmentally toxic solvents applied in the process. Furthermore, heating inorganic acids produces toxic gas emissions of $SO_x$ and $NO_x$ [52]. Long reaction times also mean that more energy is required to maintain the long heating time. This reduces the benefits of the low operational temperatures.

### 3.3.2 Near- and supercritical fluid technology

There has been an increased attention towards supercritical fluids (SCF) as environmentally friendly solvents for a wide range of applications. SCF's are for instance utilized for extractions, material processing, chemical reactions, and degradation of different materials among other applications [53].
Near-or supercritical fluids add a new dimension to conventional solvents, as the properties can easily be tuned to the process needs by changes in temperature, pressure and composition. Theoretically, any fluid can under the correct conditions become a SCF. The correct conditions depend on their critical temperature and pressure, which are different from each fluid. Critical temperatures and pressures for some common substances are listed in Table 3.

Table 3. Critical points of some common fluids [54]

| Liquid | $T_c$ /°C | $P_c$/MPa |
|---|---|---|
| Ethane | 32.18 | 4.87 |
| Propane | 96.68 | 4.25 |
| Carbon dioxide | 30.97 | 7.38 |
| Pentane | 196.6 | 3.37 |
| Acetone | 234.95 | 4.70 |
| Methanol | 239.5 | 8.10 |
| Ethanol | 240.75 | 6.14 |
| Benzene | 288.90 | 4.89 |
| Water | 373.95 | 22.06 |

The fluids can be classified as low-critical temperature ($T_c$) fluids or high-critical temperature ($T_c$) fluids [53]. Condensable gasses, such as: $CO_2$, ethane and propane are examples of low critical temperature solvents. High critical temperature solvents include alcohols, alkanes, water etc. The solvent power of SCF's is different from each other. The solvent power of high $T_c$ solvents is considered as being significantly higher than low $T_c$ solvents. This means that high $T_c$ solvents are considerably better solvents for high molecular weight materials, such as polymers, as they can degrade the crosslinked-bonds of thermoset polymers [53]. The near-and supercritical fluids used during the investigations in this thesis are therefore exclusively high $T_c$ solvents.

SCF's possess considerably different physicochemical properties than at ambient conditions. This includes properties that are in-between those of a gas and a liquid. Water is one of the most used and investigated supercritical fluid. The phase diagram and physicochemical properties of water is shown in Fig. 12 and Table 4.

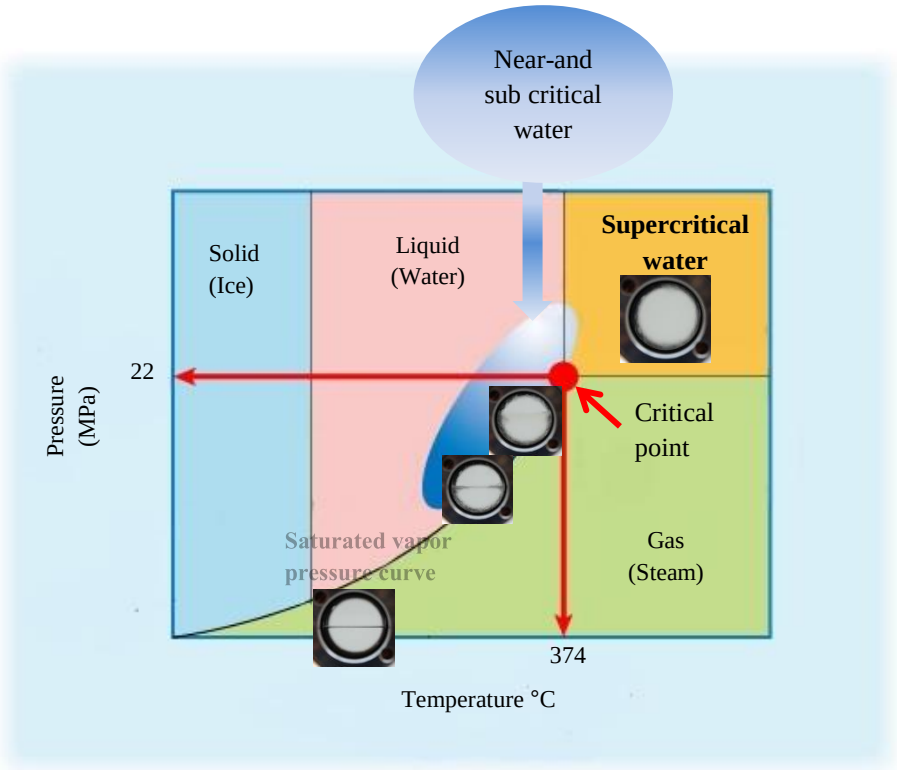


*Fig. 12 Phase diagram for water [55]*

Upon increase in temperature and pressure along the vapor-liquid equilibrium curve, both phases coexist. With a further increase in temperature and pressure, the phases become less distinguishable (obtaining similar density), until the critical point is reached. Only one phase is present at this temperature and pressure (T = 374 °C, p = 218 bar).

*Table 4. Physiochemical properties water at ambient, subcritical and supercritical conditions [56]*

| | $Water_{Ambient}$ | Subcritical water | Supercrit. Water | |
|---|---|---|---|---|
| T [°C] | 25 | 250 | 400 | 400 |
| p [MPa] | 0.1 | 5 | 25 | 50 |
| ρ [g $cm^{-3}$ ] | 0.997 | 0.80 | 0.17 | 0.58 |
| ε | 78.5 | 27.1 | 5.9 | 10.5 |
| $pK_w$ | 14.0 | 11.2 | 19.4 | 11.9 |
| $c_p$ [kJ $kg^{-1}K^{-1}$] | 4.22 | 4.86 | 13 | 6.8 |
| η [mPa·s] | 0.89 | 0.11 | 0.03 | 0.07 |
| λ [$mWm^{-1}K^{-1}$] | 608 | 620 | 160 | 438 |

The density ρ decreases as the temperature and pressure reach the supercritical state, cf. Table 4. These changes in density correlate with other macroscopic properties to reflect changes at the molecular level. This includes solvation power, degree of hydrogen bonding, polarity, dielectric strength, diffusivity and viscosity [57].

The static dielectric constant ε is a measure of the relative effectiveness of water as an electrical insulator. The value is related to the degree of interaction between the water molecules, the dipole moment and the polar orientations. At 25 °C, water has a relatively high dielectric constant of 78.5, meaning that the polar water molecules are positioned close to each other with hydrogen bridges build to each other. The solubility of polar and ionic inorganic substances in water is therefore high at ambient conditions. This value drops to approx. 6 just above the critical point, because the structure of water changes and most of the intermolecular forces are broken to around one third of that at standard conditions [58]. These changes influence the solvation behavior of water as it becomes less polar and more like organic solvents. Thus, the dissolution of otherwise hydrophobic organic compounds in water increases and the solubility of polar and ionic inorganic substances decrease [58-61].

The ionization constant of water $K_w$ (Eq. 2) is represented with the equilibrium equation (Eq. 1).

$$H_2O_{(aq)} + H_2O_{(aq)} \leftrightarrow OH^-_{(aq)} + H_3O^+_{(aq)} \quad (1)$$

$$K_w = [OH^-_{(aq)}] \cdot [H_3O^+_{(aq)}] \quad (2)$$

$K_w$ depends largely on density and temperature. Therefore, this constant can be used to govern the chemical reactions occurring in the water in favor of ionic or free radical reactions by changing temperature and pressure. At $pK_w \leq 14$, water is more suitable as medium for heterolytic reactions and at $pK_w \geq 14$ more homolytic reactions takes place [56]. As an example, the pH changes from 5.6 at 250 °C to 8 at the critical point [61].

The dynamic viscosity η decreases from 0.89 mPa·s at standard conditions to 0.03 mPa·s just above the critical point, due to the increased movements of particles with high kinetic energy. This remarkable drop in viscosity results in increased diffusivity in sub- and supercritical water, which combined with high particle kinetic energies in heated water facilitate effective collisions between molecules, hence resulting in considerable increments in reaction rates [58].

Overall, these physiochemical changes in the critical region results in enhancement of mass and heat transfer processes, which is of highly interest for extracting polymer off from fibre surfaces. Several authors have found that thermosetting resin with cross-linked structure such as UP resin, phenol resin and epoxy resin was decomposed into small molecules by near- or supercritical water. Furthermore, the review paper by Morin et al. [25], report that the solvolysis technology using near or supercritical fluids is the most promising recycling technology for FRP composites.

## 3.4 SCF's to depolymerize polymers- State of the art

The use of chemical solvolysis to recycle FRP composites has been summarized in paper I as a review paper. The main conclusions from this literature review are that several factors influence the resin degradation efficiency. This includes the following; Temperature, type of reactor (e.g. batch-type of reactor or flow-type of reactor), heating time, pressure, application of catalyst/additives, reaction time, type of fluid, pre-treatment, stirring/stirring angle and composite/solvent ratio.

Temperature is the most important factor influencing the degradation efficiency. Increase in temperature results in higher degradation efficiency of the resin in all the investigations conducted in the field. Generally, temperatures between 300-400 °C were applied in the investigations conducted with water to recover the fibres and depolymerize the resin. The investigations conducted with alcohols (methanol, ethanol, propanol, benzyl alcohol and isopropanol) were in general conducted in the temperature range of 250-350 °C to recover the fibres and depolymerize the resin.

Recovery of clean carbon fibres with retained mechanical properties compared to the virgin carbon fibres was achieved in nearly all the investigations, showing that carbon fibres are able to withstand the harsh near-and supercritical environments, both using water, organic solvents and elevated temperatures. However, recovery of clean glass fibres with retained mechanical properties compared to the virgin glass

fibres has shown to be a challenge, particularly when water is used as solvent. More than 50 % loss in tensile strength was obtained in some of the investigations, cf. paper I for details. Furthermore, elevated temperatures have shown to reduce the strength of the glass fibres even more. However, when using organic solvents (e.g. methanol, acetone etc.) and thus decreasing the process temperature to recover the glass fibres, one study in the literature conducted by Kamimura et al. 2008 [62] has shown results where glass fibres were recovered with almost conserved mechanical properties compared to the virgin glass fibres. The solvent was methanol together with the catalyzing additive N,N-dimethylaminopyridine. Reaction temperature was 275 °C and the reaction time was 6 hours [62]. Almost preserved mechanical properties of glass fibres has also been achieved in the investigations conducted during this thesis in a more economic, environmental friendly and sustainable way, cf. Chapter 7 and paper III.

The use of chemical solvolysis has shown to depolymerize the polymer matrix into degradation products of varying molecular weights, depending on the reaction temperature, solvent and additives. This includes into monomers, oligomers and other chemical compounds. Nakagawa et al. 2009 [63] and Okajima et al. 2014 [64] reported that it is possible to depolymerize the polymer matrix using 1-octanol or methanol, respectively, and subsequently re-cure the resin again for reuse in new materials. Recovery of monomers (together with purification in paper VII) and identification of value-adding chemicals has been achieved in several of the investigations performed during this thesis (papers II, III, IV, V, VI and VII).

Catalyzing additives in literature have mainly been alkalis such as potassium hydroxide (KOH) and sodium hydroxide (NaOH). The use of alkaline additives has been found to be an important factor increasing the degradation efficiency considerably. Several investigations reported that it was possible to decrease the temperature and/or reaction time and still obtain the same or higher degradation efficiency than experiments without additives at similar process conditions. However, it has also been found that addition of alkaline additives generally tends to decrease the tensile strength of the recovered glass- and carbon fibres, why only small amounts should be applied, or the alkaline additives could be used together with other additives (for synergetic effects) to strengthen the depolymerization efficiency. As an example, synergistic effects of mixing additives have been reported by Liu et al. 2012 [65]. They showed that the use of a mix of phenol and KOH were much more efficient in terms of degrading the resin compared to using the additives individually. At similar temperature and pressure, the addition of only phenol (5 g) exhibited a decomposition efficiency of 14.5 wt. %, and the addition of only KOH (0.5 g) exhibited a decomposition efficiency of 28 wt. %. However, using the additives together (in amounts indicated), they achieved a degradation efficiency of 95.2 wt. %. The authors explained the increased degradation efficiency by the effect of phenoxy radicals produced from phenol, which accelerates the breaking of chemical bonds in the crosslinked matrix [65].

An investigation with the purpose of clarifying how the most employed additives in literature affects the degradation pattern of the polymer matrix was conducted, cf. Chapter 5 and paper II. The goal of this research was to extract valuable information about which degradation products the catalyzing additives produce at different temperatures, in order to gain knowledge about the process conditions where highest amounts of the valuable monomers can be extracted.

## 3.5 Summary

The use of near-and supercritical fluids to recycle FRP composites provide end-products with potentially higher value than the end-products obtained from the thermal and mechanical recycling. The technology provides recovery of long fibres with retained or almost retained mechanical properties compared to the virgin fibres. The resin is solubilized into monomers and smaller degradation products and can potentially be re-cured into new polymer materials.

However, despite the possibility to recover clean glass- and carbon fibres by chemical recycling, there are still challenges in the field. There is almost no interest in recycling GFRP composites, mainly because the value of the recovered glass fibres is low compared to carbon fibres. Furthermore, the recovery of glass fibres with decreased mechanical properties compared to the virgin glass fibres has only made the challenge even bigger.

During this Ph.D. study, several approaches have been conducted to increase the interest for recycling GFRP composites. This includes: Recovering the glass fibres with retained mechanical properties, recovering purified monomers, recovering a fuel oil and petro-chemicals, all in a sustainable, economic and efficient manner. The most important findings will be summarized in the following chapters, including a brief description of the experimental equipment used during the project.

# 4. Experimental Equipment

Depolymerizing the polymer matrix and recovering the fibres were conducted in high temperature high pressure laboratory scale batch reactors. In this chapter, the reactors used during the Ph.D. study will be described.

## 4.1 Batch reactor design I

Fig. 13 illustrates the batch reactor applied for the majority of the investigations conducted in this thesis. The reactor is none-stirred and has a volume of 280 mL and constructed in 316 stainless steel (BC-1, HIP - High Pressure Equipment, USA). The reactor is heated with an electrical heating mantle to a maximum temperature of 350 °C and a pressure rating of 300 bar. The pressure is read manually from the manometer. The temperature is measured by a Pt-100 temperature measurement device which is connected to a PID control unit which adjusts the effect of the heating mantle. The thermocouple is placed in a thermowell very close to the center of the reactor vessel. The small wall thickness of the thermowell allows for fairly precise temperature measurements. The maximum heating rate was 5 °C/min. The inside diameter of the reactor vessel was 60 mm and the depth of the reactor was 155 mm. Sampling could only be conducted through one valve (cf. PI-diagram in Fig. 13 right).

Since the composites were solid pieces measuring up to 100×40×10 mm it was necessary to load the composite specimen into the reactor before initiating the experiments. Solvent and additives were also added together with the composite specimens. This was conducted by removing the top part of the reactor manually. The reactor was then sealed with 6 screws using a torque wrench. After the reaction time, the heating mantle could be removed manually to allow faster cooling by natural convection (approx. 2 h). The liquid reaction products were then removed from the reactor by pouring the content into blue cap flasks. Fibres were removed manually. The reactor system was rinsed several times using acetone.

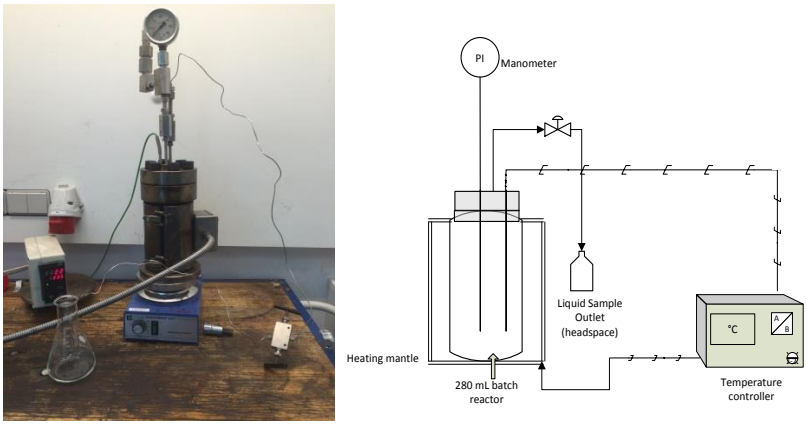


*Fig. 13 left: 280 mL batch reactor (design I) with an electrical heating mantle. Right: PI-diagram of reactor design I.*

## 4.2 Batch reactor design II

Fig. 14 illustrates batch reactor design II. The reactor is a 1 L none-stirred high pressured batch reactor constructed in 316 stainless steel (Series 4650, model 4653 High Pressure Reactor, Parr Instruments, USA). The reactor has an inside diameter of 60.35 mm and a depth of 330.35 mm and was heated by an electrical ceramic heater (model 4926, Parr Instruments USA). The temperature inside the reactor was measured by a T316 thermocouple placed in a 340.29 mm deep thermowell from the top of the reactor and connected to an electrical temperature controller (model 4838, Parr Instrument USA). The pressure was measured manually by a manometer and digitally by a pressure transducer connected to the reactor controller. The sampling and gas inlet valves are shown in the PI- diagram in Fig. 14 right. Sampling from the bottom of the reactor was performed through valve G2 or G3 and from the headspace through valve G4. Similarly as the experiments performed with reactor design I, it was necessary to load the solvent, composites and additives directly into the reactor by removing the top part of the reactor prior to the experiment. The reactor was subsequently closed with a split-ring closure with 8 cap screws using a torque wrench. The reactor was then manually lifted into the ceramic heater. The heating rate could be controlled to either slow (5 °C/min) or fast (10 °C/min) heating.

After the reaction time, the reactor was cooled down by natural convection inside the ceramic heater overnight (approx. 15-20 h). Removal of the reaction products was conducted manually by removing the reactor from the ceramic heater and loosening the 8 cap screws. The liquid reaction products were loaded into 500 mL blue cap bottles and the recovered fibres were collected manually with tweezers. The whole reactor system was then rinsed with acetone and water several times. Due to the size

of the reactor system, the last steps (product removal and rinsing) were performed outside the fume hood. Therefore, it was necessary to wear gas masks due to a very strong smell and health risks related to the reaction products.

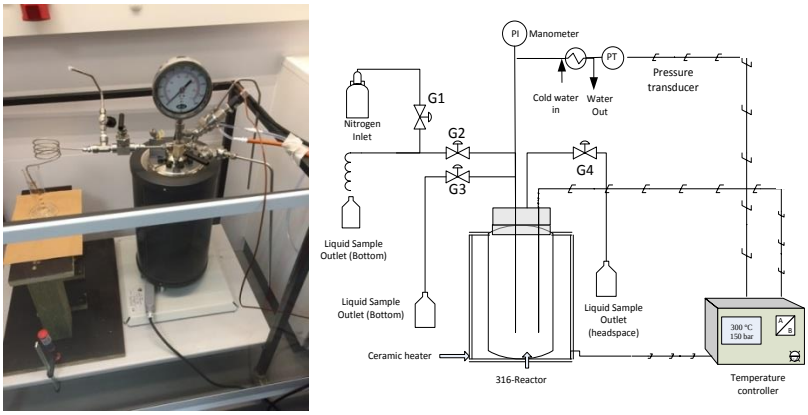


*Fig. 14 left: 1 L batch reactor (design II) with ceramic heater. Right: PI-diagram of reactor design II.*

## 4.3 Batch reactor design III

Experiments were also conducted using a microwave oven (Anton Paar Microwave Pro, Rotor 8N) (Fig. 15) to assess the feasibility of degrading the polymer matrix and recovering the fibres with microwaves.

The microwave oven is equipped with two standard magnetron sources of 850 W for generation of microwaves (maximum power 1500 w) and a rotor (390 mm × 320 mm) with space for 8 pressure reaction vessels, either in quartz (NXQ80) or polytetrafluoroethylene (PTFE) ceramic (XF100). The XF100 Teflon vessels with a pressure limit of 60 bar and a temperature limit of 260 °C was used in the investigations. The volume of each vessel was 100 mL (min. filling vol. 6 mL max. filling vol. 50 mL).

Composite specimens (2-6 gram) were poured into four available reaction vessels together with the solvent. The vessels were then placed in a protective casing, cf. Fig. 15 right and closed carefully with lip-type seal caps. A protective casing is also put onto the cap. To ensure uniform temperature distribution during the run, the rotor was loaded symmetrically. The vessels were then fixed by symmetrically screwing down the upper plate of the rotor until the vessels could not be moved. After placing the rotor lid, the loaded rotor was placed into the microwave.

After the reaction time and cooling, the rotor was removed into a fume hood to avoid vapors released from the degraded resin and sulphuric acid ($SO_x$). The products were

poured into blue cap bottles and the reactor vessels were cleaned by acetone and water. If necessary, a washing program was used to remove residue from the walls of the vessels.


*Fig. 15 left: Microwave oven. Right: Rotor and Teflon reaction vessels.*

# 5. Depolymerization of the polymer matrix

Depolymerizing the polymer matrix is necessary in order to liberate and recover the fibres. The degree of depolymerization, the speed of the depolymerization reactions and particularly the nature of the produced degradation products have been found to primarily depend on following parameters.

- Temperature
- Nature of solvent
- Additives
- Reaction time

The findings in all the papers with regards to degradation products from UP resin are summarized in this chapter.

## 5.1 Effect of temperature and catalysts

The effect of temperature, solvent and catalyst was investigated in paper II and with the use of batch reactor design I. The degradation of UP resin was investigated at temperatures of 200, 250, 275, 300 and 325 °C at a constant pressure and reaction time of 300 bar and 30 min, respectively. The solvent was water in the absence (experiments abbrev. A) or presence of additives (KOH/phenol mix, experiments abbrev. B) and (KOH, experiments abbrev. C). The degradation products produced by means of the different conditions was identified by GC-MS. The chromatograms and an overview of the reaction products produced are shown in Fig. 16 and Fig. 17, respectively.

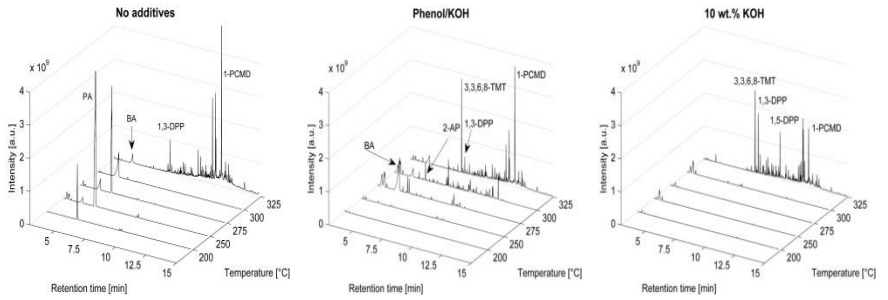


*Fig. 16 GC-MS chromatograms for all the experiments at 200-325 °C with/without additives. Abbreviations: Benzoic acid: (BA), phthalic anhydride: (AP), 1,3-diphenylpropane: (1,3-DPP), 1,5-diphenyl, 1-pentene,: 1,5-DPP), 1-propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl: (1-PCMD), 3,3,6,8-tetramethyl-1-tetralone: (3,3,6,8-TMT), 2-allylphenol: (2-AP)*

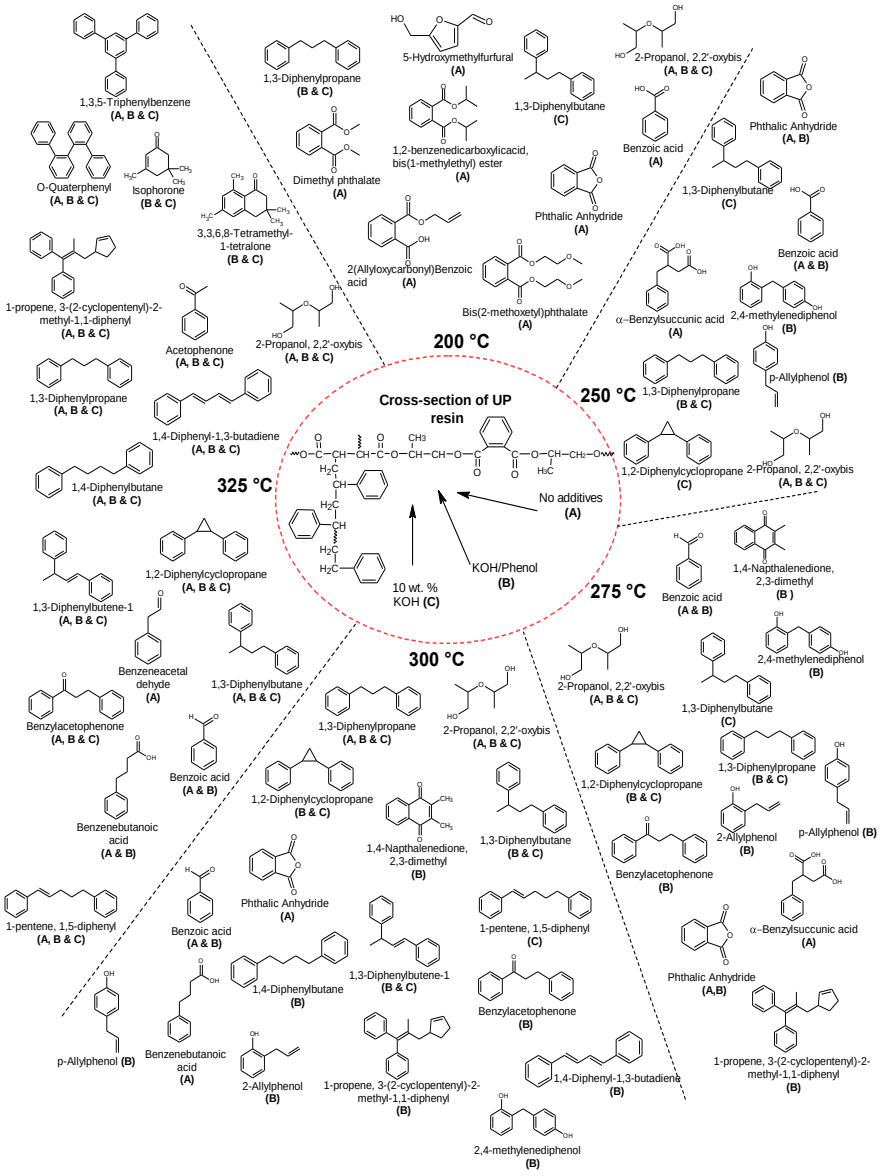


*Fig. 17 Overview of the degradation products produced by the hydrolysis of UP polyester resin at different temperatures and by the influence of the additives KOH/phenol (B) and 10 wt. % KOH (C) and the reference experiments without additives (A).*

Based on the GC-MS investigations of the liquid product from experiments conducted in the absence of additives, few and small amounts of degradation products was identified in the temperature range of 200-300 °C. Those identified in largest amounts were the monomer phthalic anhydride and benzoic acid (cf. chapter 6 for details about recovery of monomers).

In the experiments conducted with the additive KOH, the variety and amount of identified compounds was also low in the temperature range of 200-300 °C (Fig. 16 and 17). However, the use of the additive blend phenol/KOH seemed to accelerate the depolymerization of UP resin at lower temperatures, as considerably more degradation product was identified already at 275 °C. Although very few degradation products was identified at 300 °C in the absence of additives (A) and in the experiments with KOH (C), 92 % and 85 % of the resin was degraded and removed from the surface of the fibres, respectively (cf. paper II for details). This indicated that the polymer has been degraded into high molecular weight degradation products (oligomers), which cannot be easily analyzed by GC-MS.

Similar observations were made in previous investigations conducted in the beginning of the PhD study (not a paper). A GFR epoxy composite was used for the experiments. Alkaline water, adjusted to pH 12 with KOH, was used and the process temperature and pressure was 235 °C and 300 bar. A rather low temperature was chosen, in order not to completely degrade the resin into small degradation products. The reaction time was 30 min starting after reaching the temperature set point. After the hydrolysis process, the glass fibres were still completely covered with resin, cf. Fig. 18 A.

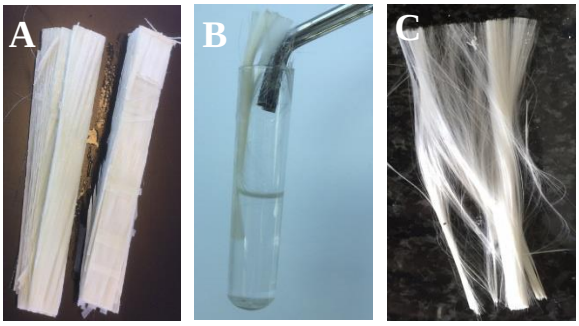


*Fig. 18 Results from the hydrolysis of a GFR epoxy resin composite. A: After the hydrolysis process. B: Treatment in acetone. C: After treatment in acetone for 24 h.*

The glass fibres covered with resin were left in acetone for 24 h, resulting in complete removal of the polymer and recovery of clean glass fibres (Fig. 18 C). As it can be observed in Fig. 18 B, the polymer precipitated at the bottom of the test tube as small fractions of un-depolymerized polymer particles, which could easily be

separated from the acetone by filtration. GC-MS analyzes of the liquid product showed very few degradation products, similarly as obtained in the experiments without additives and with the additive KOH at 200-300°C (cf. paper II).
This experiment confirms that the fibres can either be recovered by degrading the polymer matrix into small fractions of undepolymerized particles or into smaller degradation products soluble in the reaction liquid. Thus, temperature and the presence/absence of additives control the degree of depolymerization.

At 325 °C, the degradation products seemed more or less similar in all the experiments, independent of the additives (cf. Fig. 17). A comparison of the compounds identified at 200-300 °C and at 325 °C shows that the majority of the compounds are similar, except from a group of compounds which were only identified at 325 °C, called polyphenyls. They are crystalline aromatic hydrocarbons that contain a sequence of four benzene rings in the molecule and are widely used laser dyes for the near UV to violet part of the spectrum [66]. The fact that they were not identified at lower temperatures despite the presence of additives indicated that their production cannot likely be enhanced by additives but exclusively by providing additional energy in the form of heat to the system. Several isomers of polyphenyls were found in all the experiments (at 325 °C) and considered as reaction products from the styrene chain, cf. Fig. 19 for structures. All the isomers were found with reverse match factors (RMF) in the range of 837 to 946. The matching factors reported by the MS search program are between 0 (no match) and 1000 (perfect match), meaning that the identifications were of high quality.

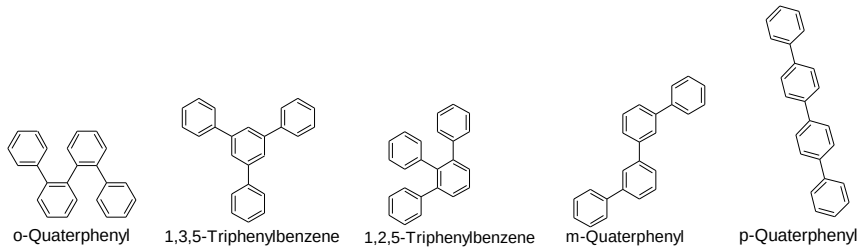


*Fig. 19 Structures of polyphenyl isomers identified in all the samples at 325 °C and 300 bar.*

The identifications of polyphenyls have been compared to another study in the field of cosmochemistry. Callahan et al. 2013 [67] irradiated benzene at 19 K by 0.8 MeV protons. The organic residue left from the irradiation was analyzed by GC-MS. The authors identified polyphenyls with up to four rings, including 1,3,5-triphenylbenzene and 1,2,5-triphenylbenzene, similarly as identified in our study (paper II) after hydrolysis of UP resin composites at 325 °C. The purpose of their work was to compare the products from irradiated benzene with the compounds identified in extracts from the Murchison and Orgueil meteorites. They concluded that their results are consistent with the possibility that solid phase radiation

chemistry of benzene (from icy mantles of interstellar dust grains) produced some of the complex aromatics found in meteorites [67].
This comparison confirms the fact that complex chemistry is also governing at elevated temperatures ≥ 325 ° in our study; however in our case in near critical water conditions without irradiation, meaning that radical chemistry probably is involved in both cases.

## 5.2 Nature of solvent

The selection of solvent has mainly been based on an environmental and economic perspective and partly based on Hansen's Solubility Parameters (HSP). HSP is a tool for predicting the solubility of a polymer in solvents and solvent blends. At ambient conditions, solvent selection will exclusively have been based on HSP. However, since the chemical degradation process is conducted at high temperatures and high pressures, HSP can no longer be used as efficiently to select a solvent. To understand why, the theory behind HSP will be summarized briefly.

### 5.2.1 Hansen's Solubility Parameter (HSP)

Prediction of the polymer solubility is based on the cohesive energy of liquid, which is the energy required to convert a liquid to a gas. The energy of vaporization is a direct measure of the total (cohesive) energy holding the molecules of the liquid together, and consists of the contribution of three kinds of interactions:

- Nonpolar, atomic (dispersion) interactions (D)
- Molecular, dipolar interactions (P)
- Molecular, hydrogen bonding interactions (H)

The basic equation governing the assignments of Hansen Parameters is the total cohesion energy E and can be written as the sum of the individual energies:

$$E = E_D + E_P + E_H \tag{3}$$

Diving Eq. 3 by the molar volume, the square of the total solubility parameter which is also called the Hildebrand parameter can be observed. Thus the Hildebrand solubility parameter is the sums of squares of the Hansen D, P and H components, cf. Eq. 5. [68].

$$\frac{E}{V} = \frac{E_D}{V} + \frac{E_P}{V} + \frac{E_H}{V} \tag{4}$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{5}$$

As described in the section about near- and supercritical fluids, Section 3.3, the physico-chemical changes of e.g. water is to a great extend a consequence of the

diminishing hydrogen bonding interactions. At ambient conditions, the Hildebrand parameter of water is 48 $MPa^{0.5}$. Compared to the Hildebrand parameter of a styrene cross-linked UP resin consisting of propylene and maleic anhydride (sty/prop/MA) (22.2 $MPa^{0.5}$), their Hildebrand parameters is far from each other, indicating very low solubility at ambient conditions. However, upon increasing the temperature and pressure, the Hildebrand parameter of water decreases down to 28 $MPa^{0.5}$ at 325 °C and 300 bar, cf. Table 5. The solvency behavior of water becomes similar to that of acetone (19.9 $MPa^{0.5}$ ambient). Therefore, water could be considered as a better option for composite degradation than organic solvents, because it is more environmentally friendly, cheap and non-toxic. The disadvantage of using water instead of e.g. acetone is the high heat capacity, which means higher energy consumptions to heat up the water.

Although HSP was not used to select the near-or supercritical fluids, the tool was used to select solvent for washing the fibres subsequent the high temperature high pressure treatments. The residue on the surface of the fibres was considered as sty/prop/MA and degradation products thereof (Hildebrand parameter of 22.2 $MPa^{0.5}$). The Hildebrand parameter of this residue is considered close to that of acetone. Therefore, acetone was used to wash the glass- and carbon fibres after every treatment, providing a very efficient fibre washing procedure.

*Table 5. HSP values for sty/prop/MA polymer, acetone and water at ambient conditions and in the temperature range 200-325 °C at 300 bar [69-70]*

| Polymer /solvent | Temperature [°C] | Pressure [bar] | Hildebrand parameter ($MPa^{0.5}$) |
|---|---|---|---|
| Sty/prop/MA | - | - | 22.2 |
| Acetone | Ambient | Ambient | 19.9 |
| Water | Ambient | Ambient | 48 |
| Water | 200 | 300 | 39.5 |
| Water | 250 | 300 | 36 |
| Water | 275 | 300 | 33.5 |
| Water | 300 | 300 | 32 |
| Water | 325 | 300 | 28 |

### 5.2.2 Increasing the solvency behavior of solvents

Based on the investigations conducted in paper IV and paper VIII, it has been found that the solvency power of a solvent can be increased considerably, either by recycling the solvent (paper VIII) or increasing the composite/solvent ratio (paper IV). The effect of recycling the solvent was investigated in paper VIII. Acetone was used as solvent and the GFR composites were epoxy based. Since the experiments were conducted exclusively to investigate the effect of solvent recycling, the process temperature was rather low (240 °C), meaning that the glass fibres were not recovered, cf. paper VIII for details.

It was possible to recycle the acetone for 8 experiments, using a new composite specimen for each experiment and without adding new supplies of acetone. Each time the acetone was recycled, the color became darker and the composite specimen seemed to be more degraded, cf. Fig. 20 and Fig. 21. After exp. 8, the acetone was completely black and more viscous than pure acetone. FT-IR analyzes of the black dried recyclate obtained after exp. 8 showed nearly 70 % match with bisphenol A epoxy resin, cf. paper VIII for spectrum. This could indicate that the Hildebrand parameter of the recycled acetone approaches the Hildebrand parameter of the epoxy matrix, and that the solvency power of recycled acetone towards epoxy resin increases. Furthermore, the gradual increase in the concentration of monomers and degradation products in the acetone might also act as catalyzing additives and participate in the degradation of the polymer matrix.

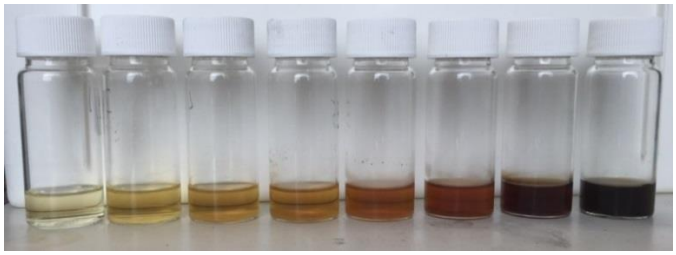

*Fig. 20 Appearance of acetone after 1-8 recycles from left to right.*


*Fig. 21 Appearance of composites subjected to acetone recycled from 1 and up to 8 times.*

Increased solvency behavior of acetone was also observed in paper IV, by increasing the composite mass/solvent volume ratio, as mentioned previously. Similarly as in the acetone recycling experiments, the degradation products became considerably more up-concentrated and could have acted as catalyzing additives.

In an environmental and economic perspective, the solvolysis process becomes more sustainable. Considerably amounts of solvent can be saved and no catalyzing additives are necessary. Other benefits are the fact that temperature and pressure also are lowered, meaning that the process design of e.g. a larger scale plant could be cheaper. Instead of a pressure at 300 bar, a pressure of 60 bar is enough. Furthermore, the acetone left can easily be distilled and re-used, as shown in paper IV.

## 5.3 Summary

Following points summarize the most important findings related to the depolymerization of the polymer matrix.

- The fibres can be recovered by complete depolymerizing of the polymer matrix into monomers and smaller degradation products or a partial depolymerization of the polymer matrix into smaller fragments of un-depolymerized particles. Complete depolymerization requires higher temperatures than partial depolymerization.

- Temperatures at 325 °C produces a compound group (polyphenyls) which was not observed at temperatures ≤ 300 °C. The presence of polyphenyls confirmed the fact that complex chemistry is governing at elevated temperatures (homolytic or heterolytic reactions).

- The solvency behavior of a solvent towards the polymer matrix can be increased by either recycling the solvent several times or by increasing the composite/solvent ratio. The up-concentrated degradation products might potentially act as catalyzing additives.

# 6. Recovery of monomers

## 6.1 Background

In a material-to-material recycling perspective, recovery of monomers from the polymer matrix is considered valuable, why it was one of the goals during this PhD study. Paper II, V, VI and VII deals with the recovery of particularly the monomer phthalic acid from composites with UP resin as the polymer matrix.
Recovery of the monomers from the polymer matrix has been found to depend strongly on several parameters. The most important includes:

- Temperature
- Nature of solvent
- Additives

It is crucial to acquire knowledge about the process conditions at which the monomer is released from the polymer matrix and the process conditions at which the monomers starts to decompose again. Such information will provide a window, where recovery of highest possible amounts of monomer can be expected. The selection of solvent and additives has also shown to affect the recovery of monomers considerably.

## 6.2 Results

Initial investigations were conducted to attain a wider knowledge about the effect of temperature, solvent and additives on the nature of degradation products and recovery of the monomer phthalic acid. Experiments were conducted using batch reactor design I and II and the composites were reinforced with glass fibres which were held together with UP resin as matrix.
Fig. 22 shows an overview of the studies performed during this PhD study, which was related to the recovery of phthalic acid and the outcome of the study. The use of alcohols such as ethanol or propanol (paper VI) degrades the resin and recovers phthalic acid, based on GC-MS investigations. However, alcohols are not the best solvent for phthalic acid recovery, because it was found that the monomer reacted with the alcohols, producing diethylphthalate and dipropylphthalate through Fischer esterification reactions, cf. Fig. 23.

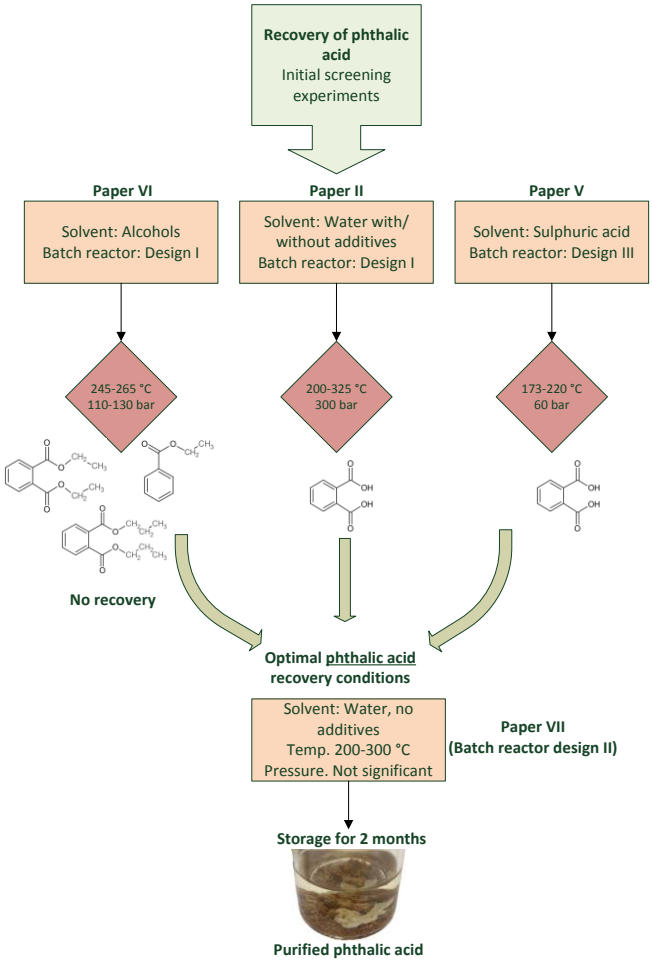


*Fig. 22 Flow chart showing the studies performed and the outcome in terms of phthalic acid recovery.*

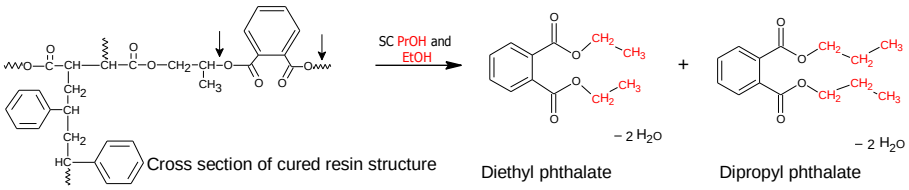


*Fig. 23 Production of diethyl phthalate and dipropyl phthalate through Fischer esterification of phthalic acid with ethanol and 1-propanol.*

The use of sulphuric acid with concentrations in the range of 1-7 M (paper V) and temperatures in the range of 173-220 °C recovered phthalic acid in its original form. These observations were interesting from a scientific point of view. However, from an industrial point of view (ex. up-scaling), the use of sulphuric acid is not a preferred solvent, due to particularly corrosion on equipment and development of hazardous gases.
The use of water as solvent is considered much more safe and cheap. The investigations conducted in paper II was conducted with water and additives such as potassium hydroxide (KOH) and a mix of KOH/phenol. The use of water without additives recovered phthalic acid in the liquid phase, found by GC-MS. When additives were added, recovery of phthalic acid was not achieved.
Based on the results from paper II, a new study was initiated using batch reactor design II (paper VII) using water without additives at temperatures in the range of 250-350 °C. In-situ sampling at 250, 275, 300, 325 and 350 °C was conducted during the heating time. A brown precipitate was observed at the bottom of the liquid samples after few hours. The samples were stored for additional 2 months in dark without separating the liquid phase from the precipitate. This resulted in the recovery of nearly purified white fractions of phtalic acid (cf. Fig. 22 and paper VII) which could easily be separated from the liquid and the remaining precipitate by a tweezer. FT-IR and GC-MS silylation investigations revealed that the majority of the precipitate collected at 250-325 °C was composed of phthalic acid.

The precipitation of nearly purified phthalic acid facilitates easy separation and purification of the monomer. However, in order to recover the majority of the phthalic acid from the polymer matrix, a different procedure is necessary. A suggestion includes heating the reactor to approx. 275-300 °C without any further temperature increase. For every 10-15 min, sampling should be conducted, in order to extract phthalic acid from the process continuously as the monomer is released from the matrix. This will also minimize that too long residence time inside the reactor will decompose the monomer. If necessary, additional heated water can be pumped into the reactor to complete the recovery of the fibres.

## 6.3 Summary

Considering the goals put up in the beginning of the thesis (Fig. 4), it can be concluded that goal number three can be accomplished in terms of UP resin degradation. Phthalic acid can be recovered using water as solvent without the use of additives. Furthermore, by storing the liquid collected from the reactor at temperatures in the range of 250-325 °C, 92-97 % (based on composition) phthalic acid precipitated.

# 7. Recovery of Fibres

## 7.1 Background

Recovery of the fibres has been the main focus area in the majority of the investigations conducted in the field of chemical degradation of FRP composites. Particularly the carbon fibres have been of interest in the majority of the studies, due to the higher value compared to glass fibres and because carbon fibres have become a commercial interest. Furthermore, manufacturing of carbon fibres are the most environmentally impacting in a composite [71].
Based on the literature study performed during this PhD on chemical degradation of FRP composites (paper I), the carbon fibres can be recovered with retained or nearly retained mechanical properties, whereas the glass fibres loose up to 60 % of the mechanical properties. However, with more than 90 % of FRP composite waste being GFR composites [72], one of the major considerations from the beginning of this project was to develop a sustainable and economically viable method to decompose the polymer matrix of GFR composites and recover the glass fibres with retained or almost retained mechanical properties. The investigations conducted in paper III propose a method where this has been achieved.

## 7.2 Results

The experiments were conducted using hybrid fibre composites with an epoxy matrix and batch reactor design I, in order to investigate the impact of the solvolysis process on both glass- and carbon fibres. It was possible to recover the fibres in water at temperatures and pressures in the range of 280-300 °C and 300 bar and reaction times of 0-60 min. The experiments were performed by loading the reactor with the composite and approx. 235 mL water, resulting in a completely filled reactor. This induced a pressure above 300 bar already during the heating process. To keep a pressure of 300 bar (the pressure rating of the reactor), depressurizing the system was necessary. Therefore, it was necessary to control the system continuously. Optimizing the process with the main purpose of avoiding depressurizing the system was considered. Instead of loading the reactor completely with water, the amount of water was decreased down to 45-110 mL. The initial thoughts are illustrated in Fig. 24. The first image (Fig. 24 A) represents the filled reactor, and therefore a composite completely covered with water inside the reactor (100 % covered). The amount of water used for the hydrolysis process was then decreased until corresponding to 75 % (Fig. 24 B), 50 % (Fig. 24 C) and 25 % (Fig. 24 D) coverage of the composite specimen inside the reactor. Recovery of fibres was achieved in all the experiments, despite the lower amount of solvent and lower pressure compared to a filled reactor.

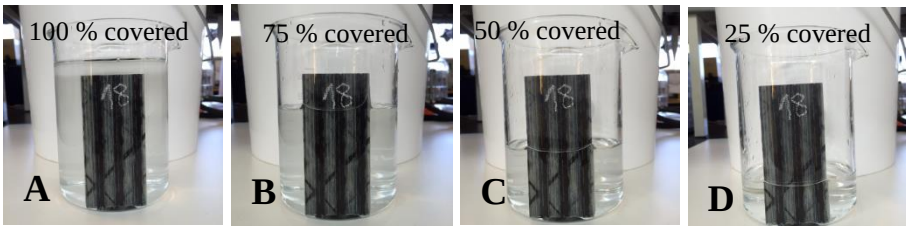


*Fig.24 Illustrations showing the idea behind adjusting the composite/solvent ratio according to the degree of solvent covering the composite specimen.*

Similar process conditions, but with acetone as the solvent was also investigated. The use of only 27 mL acetone (15 % coverage of the composite specimen) was enough to degrade the resin and recover the fibres, cf. Fig. 26C and Fig. 26D for photos and SEM images of the acetone recovered glass-and carbon fibres. Comparison of the recovered glass fibres with the virgin glass fibres (Fig. 26 A), it is clear that the sizing on the surface of glass fibres recovered using both water (Fig. 26B) and acetone has been removed by means of the chemical treatments. The virgin glass fibres have a reflecting surface and the individual fibres are bundled in large numbers due to the sizing, which makes it easier to handle the glass fibres. The recovered glass fibres were fluffy and not bundled together. The purpose of sizing is not only to make the fibres easier to handle. The performance of sized glass fibres is also improved, because the fibres are protected so that they remain undamaged during processing and manufacturing [73]. Sizing is therefore crucial.

Glass fibre sizing is not a single chemical compound, but a mixture of several complex compounds. Although little is known about the sizing due to commercial recipes by manufactures, Liu et al. 2008 [74] has proposed a structure. Fig. 25 shows a simplified illustration of the sizing layer. The primary components are the film former and the coupling agent. The purpose of the coupling agent, which is often an organosilane compound, is primarily to bind the fibre to the matrix resin. The coupling agent possesses properties which make it able to bind the hydrophilic glass fibre surface to the hydrophobic polymer (⬮). The coupling agents can also be physisorbed to the glass fibres surface (⬮). The film former (◇) serves a number of functions, which includes protecting, lubricating and holding the fibres together. Film formers are chemically similar to the matrix resin for which the sizing is designed. Beyond the two major components, sizing also consists of additional components (▭), such as lubricating agents etc. [73]

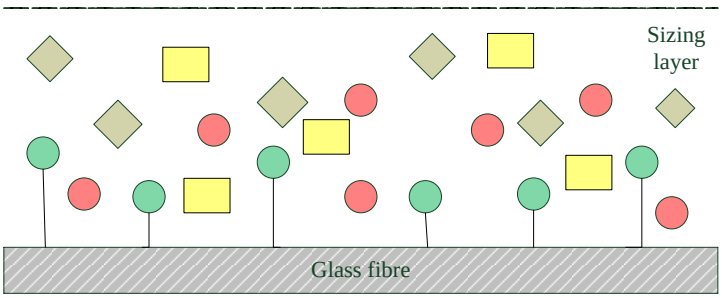


*Fig. 25 Simplified illustration of sizing layer, where ( ) represents organosilane coupling agents, ( ) represents free organosilane coupling agents, ( ) represents the film former and ( ) represents other sizing components.*

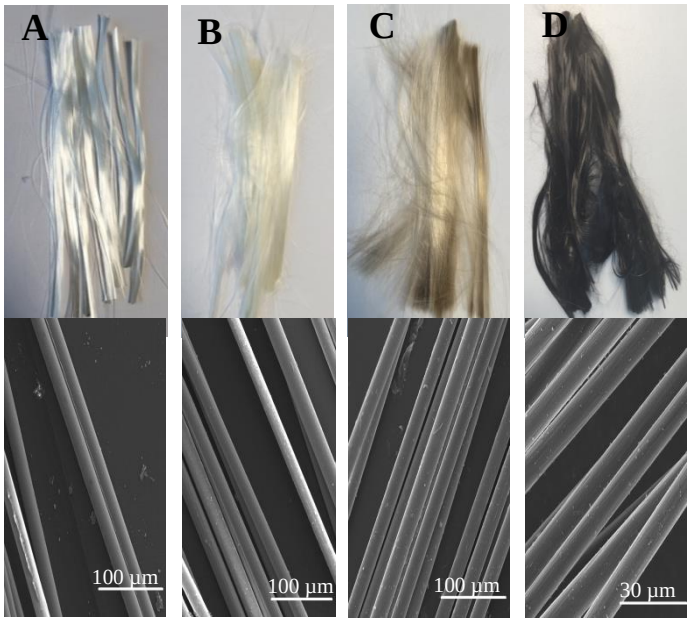


*Fig. 26 SEM images and photos of virgin glass fibres and recovered glass-and carbon fibres. a) Virging glass fibres, b) Glass fibres recovered from exp.4 with water, c) Glass fibres recovered from exp. 18 with acetone d) Carbon fibres recovered from exp. 18 with acetone.*

Removal of the sizing layer from the surface of the recovered fibres leaves the fibres more fragile and susceptible towards damage. The mechanical properties of the recovered glass- and carbon fibres were tested in paper III. In general, the tensile strength of the water- and acetone recovered carbon fibres remained similar to the tensile strength of the virgin carbon fibres, showing both chemical and thermal stability of the carbon fibres, as already shown in literature [64-65, 75-78].

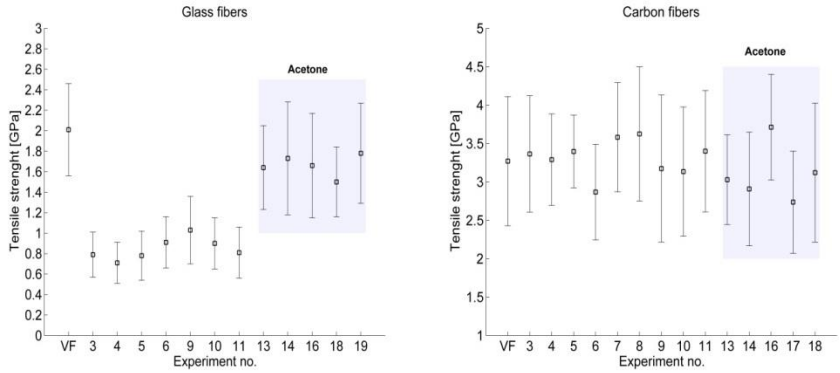


*Fig. 27 Tensile strengths of recovered glass-and carbon fibres. The marked areas represent the fibres recovered using acetone. VF represents the tensile strength of the virgin fibre.*

The glass fibres lost more than 50 % of their tensile strength by means of the hydrolysis treatment, whereas the use of acetone resulted in nearly retained tensile strengths independent of the amount of acetone loaded into the reactor, cf. Fig. 27. The use of only small amounts of acetone (27-45 mL) is therefore considered more sustainable.

However, the decreased mechanical properties of the glass fibres recovered by means of hydrolysis are not only due to the removal of the sizing layer. The major reason is the use of water as solvent. According to Maxwell et al. [79], water containing environments form a layer of water on the surface of the glass fibres. The alkali oxides present on the surface of glass fibres, such as sodium oxide, potassium oxide and aluminum oxide react with the water through the replacement of an alkali ion (e.g. $Na^+$) with a proton ($H^+$) from the water. This results in leaching of alkali ions (ex. $Na^+$) from the surface of the glass fibres and into the water layer surrounding the glass fibres. The alkali ions react with the hydroxide from the water, producing strong bases such as NaOH and KOH (Eq. 6).

$$\text{-Si-O-R} + H_2O \rightarrow \text{-Si-O-H} + R^+ + OH^- \quad (6)$$

Where R is Na, K, Ca, Mg, Al

Strong bases results in a highly corrosive environment surrounding the glass fibres, which slowly is etched. Probably, the formation of surface micro-cracks acts as stress concentrators and hence leads to reduction of mechanical properties of the fibres.

Efficient degradation of the resin using thermochemical technologies simultaneously with the recovery of type E glass fibres with retained mechanical properties is not possible using water, why the application of organic solvents is preferred.

## 7.3 Summary

Considering the goals put up in the beginning of the thesis (Fig. 4), it can be concluded that two of the goals has been accomplished.

**Low energy and solvent consumption:** Temperature and pressure at which the polymer matrix was degraded and the fibres recovered was lowered significantly from 300 °C and 300 bar down to 260-280 °C and 60-80 bar without any decrease in resin degradation efficiency, using both water and acetone. Together with the decreased energy consumption, the amount of solvent was reduced by nearly 90 % also without decrease in resin degradation efficiency.

**Recovery of glass-and carbon fibres with retained mechanical properties:**
Recovery of both glass-and carbon fibres with retained or nearly retained tensile strengths was accomplished. The reduction in temperature, pressure and amount of solvent did not affect the strengths. Therefore, the recovered fibres can potentially be reused in the re-manufacturing of new composite materials to close the loop of the FRP composite life-cycle. However, a re-sizing step could be necessary before manufacturing a new composite from the recovered fibres. The time or the facilities to conduct re-sizing has unfortunately not been available during this PhD study.

# 8. Recovery of fuel oil and other valuable petro-chemicals

## 8.1 Background

The close work in collaboration with the major wind energy companies in Denmark, such as Siemens, Vestas and LM Wind power during this study initiated considerations about the applicability of the presented technology involving a pilot scale plant to recycle composite waste in Denmark. Currently, the companies dispose the majority of their composite production waste on landfills, primarily due to Danish legislation in the field. It is not prohibited to landfill composite waste in Denmark, as it is in Germany and Sweden. Furthermore, it is the easiest and cheapest solution.

Therefore, implementation and application of the chemical solvolysis technology for recycling FRP composites in Denmark is considered negligible at the moment. In fact, the Danish company ReFiber implemented a pilot-scale plant in 2002 for recycling wind turbine blades by means of pyrolysis. They went bankrupt in 2007 due to lack of recycling materials [26].

Therefore, the implementation and application of recycling technologies such as chemical solvolysis or pyrolysis in Denmark require either changes in legislation (political changes) to force the companies to recycle their waste, or development of a recycling process with economic benefits for the composite industries and their customers, which are responsible for taking care of their wind turbine waste when wind turbines are decommissioned. Political changes require great efforts and were not considered possible during this project period, whereas development of a process with economic benefits can be investigated. These considerations initiated the idea of converting the matrix into its starting point, namely liquid fuel as an oil (paper IV).

## 8.2 Results

The studies were conducted using batch reactor design I. The solvent used was 50/50 vol. % water/acetone and the catalyzing additive KOH. The idea of mixing solvents is derived from the fact that acetone is a good solvent for UP resin and epoxy resin degradation. However, in order to minimize the costs of the recycling process, it was decided to reduce the amount of acetone by half through the use of water, too. KOH was added, because other studies reported that the use of KOH increased the resin degradation efficiency and thereby could reduce the process temperature. GFR UP resin composites was degraded in the temperature range 200-325 °C. As references,

experiments without a composite specimen and experiments without KOH was conducted. Subsequent the chemical solvolysis process, the liquid products was poured into blue cap flasks. After resting for 1 h, experiments with KOH appeared as two phases with a sharp interface, cf. Fig. 28 A and Fig. 28 B. The experiment without KOH appeared different. The organic phase appeared as a sticky oil at the bottom of the flasks instead of an upper organic phase, cf. Fig 28 D. Separation of oil from the aqueous phase was therefore also difficult.

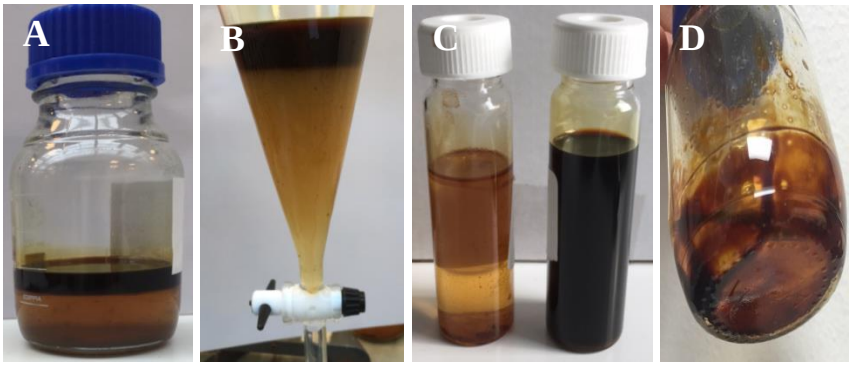


*Fig. 28 a) Appearance of the liquid product after the chemical solvolysis process with 50/50 vol. % acetone/water and KOH, b) Separation of water/oil phase from experiments with KOH, c) separated oil and water phase from experiments with KOH, d) Appearance of liquid product obtained in experiments without the addition of KOH.*

### 8.2.1 Oil quantity and properties

The quantity of oil produced by means of the chemical solvolysis is important in terms of energy balances and hence economic benefits/disadvantages. Experiments conducted using the 50/50 vol. % acetone/water mix and KOH yielded up to 41 g oil at 325 °C (based on approx. 80 g composite and approx. 118 mL acetone). Reference experiments without a composite specimen yielded similar oil quantities at 325 °C. GC-MS analyses showed that the majority of the oils produced in the pressence of KOH was composed of compounds originating from the acetone. Acetone undergoes aldol reaction with itself under alkaline conditions, producing compounds with up to 18 acetone molecules, cf. Fig. 29 and Fig. 30 [80] (paper IV).

The reference experiment without KOH yielded maximum 6 g oil. GC-MS analysis showed that the majority of the oil was composed of primarily degradation products from the styrene chain. The oil was therefore derived exclusively from the polymer matrix, cf. paper IV for styrene degradation products.

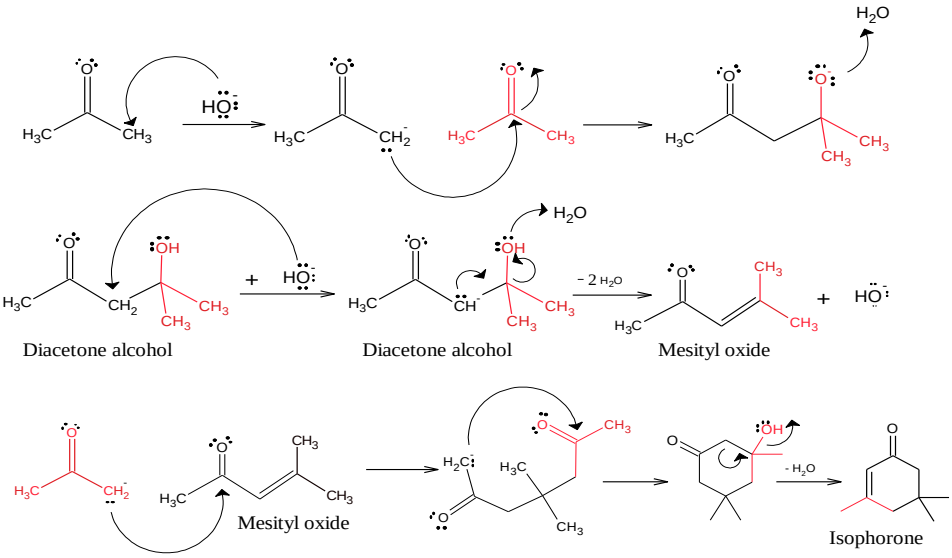


*Fig. 29 Mechanisms of an acetone aldol reaction producing isophorone [80](paper IV).*

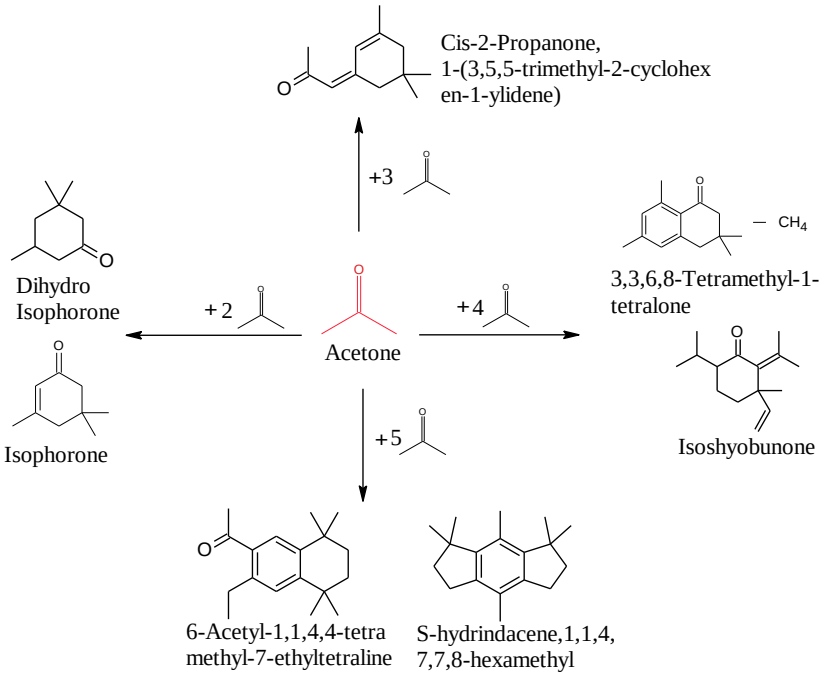


*Fig. 30 Formation of different high molecular weight compounds derived by the reaction of 3 to 6 acetone molecules [80](paper IV).*

The properties of the oils with or without KOH were similar to each other in terms of higher heating value (HHV) and ranged from 37.3 MJ/kg to 39.6 MJ/kg, which was nearly five times higher than the untreated composite specimen. Furthermore, the HHV was nearly as high as gasoline and crude oil and higher than energy sources such as hard wood, coal and bio-crude from algae's, cf. Fig. 31.

Other physical chemical and physical characteristics of the produced oils was compared with crude oil and with bio-crude and found to be more similar to crude oil than to bio-crude oil, cf. Paper IV for detailed data.

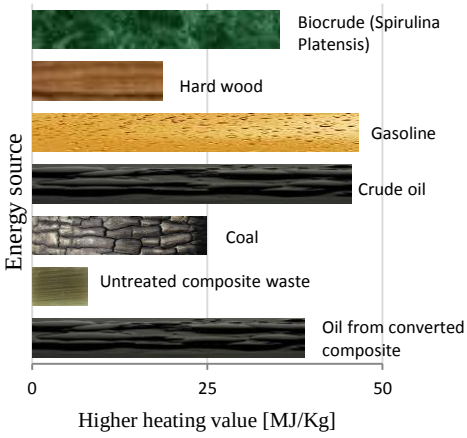


*Fig. 31 Comparison of HHV's of different energy source [80].*

### 8.2.2 Petro-chemicals

The aldol condensation reactions of acetone produce a long range of potential petro-chemicals. This includes isophorone, which is used as a chemical intermediate for synthesis of polymers, dyes, insecticides, and the like [81]. 6-Acetyl-1,1,4,4-tetramethyl-7-ethyltetralin or versalide (trade name) which is used in cosmetics, soaps, dentifrices etc. [82]. Isoshyobunone, which in a precious study by Chen et al. [83] has been extracted from *Acorus calamus* rhizomes and has shown insecticidal activity. The compound 3,3,6,8-tetramethyl-1-tetralone is according to Sigma Aldrich a part of a collection of rare and unique chemicals [84]. Due to the intense peak from this compound at 325 °C, a semi-quantitative assessment was carried out. By the internal standard method (bromobenzene), the amount was quantified to approx. 21 g/L. Considering the value of the compound at the moment (119 euro per gram), separation of the compound could increase the value of the recycling process considerably.

More than 50 different compounds were identified in the oils at 200-325 °C in either increasing or decreasing amounts (based on peak area), providing great opportunities for tailoring chemicals with industrial interest and at the same time eliminate a worldwide waste problem.

## 8.3 Energy balance

The findings of this study are interesting so far, both from a scientific point of view and an industrial point of view. However, the economic viability of the process is also crucial. Therefore, a roughly estimated energy balance was made for an up-scaled process (18.75 L) and the batch reactor design I (0.28 L). The calculations are shown in appendix A.

The energy balance, cf. Fig. 32 was calculated based on the oil yield produced in exp. 7 (solid line) and for an up-scaled process (dashed lines) at 325 °C (cf. paper IV for details). To produce 0.041 kg oil in the laboratory scale batch reactor, approx. 1 kWh was required. With a HHV of approx. 40 MJ/kg, the produced oil corresponded to 0.46 kWh of chemical energy, resulting in a negative energy balance.

The up-scaled process is calculated based on a 18.75 L, 316 stainless steel Parr reactor with a weight of 170 kg [85]. Considering that 15 kg solvent is loaded into the reactor together with 7 kg composite, the energy required heating up the reactor and the solvents was calculated. Several assumptions were made prior to the calculations, which include:

- Negligible energy loss to the environment during the heating process
- It is assumed that an up-scaled process produces similar amounts of oil compared with the laboratory scale reactor.
- The energy requirements to heat up the composite are considered negligible and not included in the calculations
- The effect of mixing two solvents is not included in the calculations

The solvent was a mixture of 50/50 vol. % acetone/water. Calculating the energy consumption to heat and pressurize this solvent mixture to 325 °C and 300 bar will be based on estimations. The heat capacity of water at ambient conditions, 4.18 J/g °C (NIST), is nearly two times higher than the heat capacity of acetone at ambient conditions, 2.16 J/g °C (NIST). Furthermore, the heat capacity of both solvents increases as they reach the supercritical state. Using NIST webbook, the heat capacity of water at 325 °C and 300 bar was found to be 5.5347 J/g °C. Data was not available for acetone. Therefore, since most energy is required to heat up water, the total energy consumption to heat up 15 kg solvent will be based on calculations on water. This will provide a value indicating the maximum amount of energy required to heat the solvents.

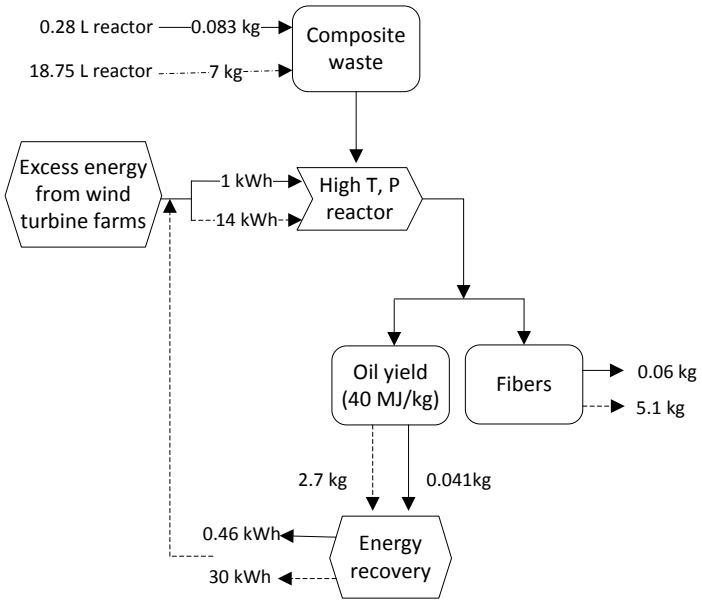


*Fig. 32 Energy balance for produced oil in batch reactor I (Using 50/50 vol. % acetone/water and KOH) and using an up-scaled reactor system.*

Based on the calculation (cf. appendix A), 7 kWh is required to heat up the solvents and 7.16 kWh is required to heat the reactor to 325 °C, resulting in a total energy consumption of 14.16 kWh. Conversion of 7.5 kg acetone and 7 kg composite produce approx. 2.7 kg oil. This amount of oil corresponds to approx. 30 kWh of chemical energy (cf. appendix A for conversion calculations), thus resulting in excess of approx. 16 kWh of chemical energy and a positive energy balance. The energy produced from the oil can either be applied to run the process or more beneficially, applied as a drop-in-fuel on refineries. The process could instead be powered by excess energy from wind turbine farms and thereby increase the sustainability of the process.

The energy consumption at 300 °C and 325 °C at pressures in the range of 200-350 bar has also been calculated based on heat capacity data of water from NIST, cf. Table 6. There is no remarkable difference in the energy required to heat the water at pressures in the range of 200-350 bar at 300 °C (Standard deviation of ± 0.3 kWh) or at 325 °C (Standard deviation of ± 0.6 kWh). Furthermore, the oil yield was not considerably affected by the pressure (cf. paper IV), why lower pressures than 300 bar can be considered more beneficial for the process. Particularly in an up-scaling point of view, as reactor, pipelines and other equipment necessary for the plant can be built with cheaper materials that do not need to withstand very high pressures.

*Table 6. Energy requirement at 300 °C and 325 °C at different pressures*

| Pressure | Energy requirement in kWh (at T = 300 °C) | Energy requirement in kWh (at T = 325 °C) |
|---|---|---|
| 100 | 6.58 (liquid) | 6.67 (vapor) |
| 150 | 6.34 (liquid) | 8.16 (liquid) |
| 200 | 6.16 (liquid) | 7.63 (liquid) |
| 250 | 6.01 (liquid) | 7.26 (liquid) |
| 300 | 5.88 (liquid) | 7.0 (liquid) |
| 350 | 5.77 (liquid) | 6.78 (liquid) |

## 8.4 Summary

The benefits of using water/acetone and KOH are not only related to the amount of oil produced, but also the practical aspect of the process. It was very difficult to handle the oil produced exclusively from the polymer matrix, as it was sticky and stuck to glassware. Therefore, separation from the aqueous phase was also troublesome. By producing an organic oil phase based on acetone derived compounds, it was possible to store the polymer oil in this organic phase. Handling of the oil was much easier, as the oil was not sticky and therefore also easily separated from the aqueous phase.

Another major benefit of using the acetone/water/KOH mixture is the production of various chemicals, which potentially can be used as petro-chemicals in other industries and increase the value of the chemical recycling process.

The last goal in terms of developing a method that can generate enough energy to make the recycling process energetically viable can be considered accomplished too. This means that additional use of fossil energy is not required and that the process can be considered more sustainable.

# 9. Conclusion

The conclusion is divided into two parts. First, a conclusion is made on the findings of this thesis, namely based on the chemical recycling process. The second conclusion is a more general conclusion about this major waste problem and consideration about how the problem can be solved worldwide.

### Chemical solvolysis as recycling technology

Chemical solvolysis as an approach to recycle fibre reinforced polymer composite waste can, based on the investigations conducted in this project and in literature, become a sustainable solution to recycle FRP composite waste. The products from the recycling process have been collected in Fig. 33 together with their potential end-applications. This includes recovery of long glass- and carbon fibres with retained mechanical properties, which can be used in new composite materials where strength is crucial. Recovery of smaller fibres can be used in lower value applications, such as filler materials in concrete or plastics. The recovered monomers can be used to produce new products or polymers.

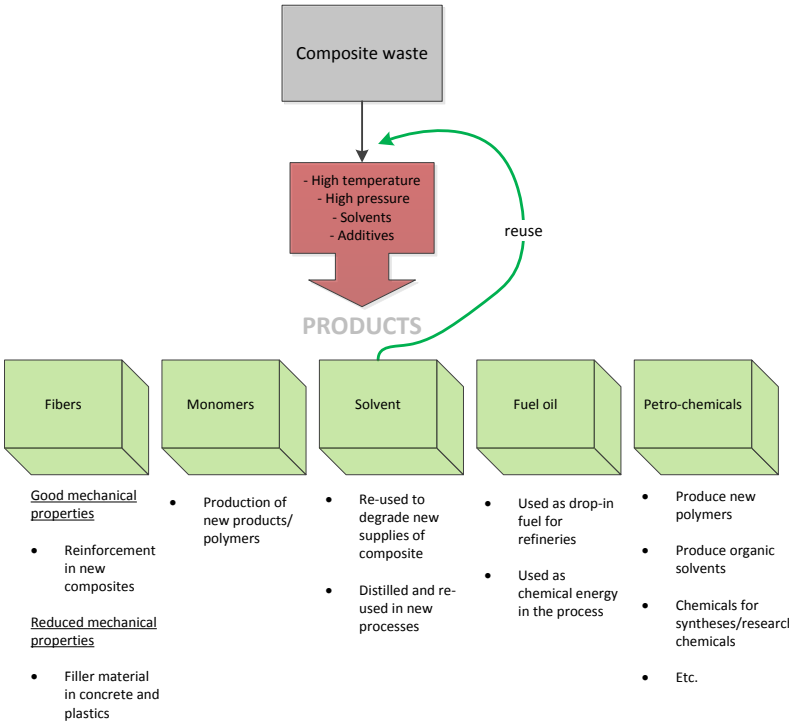


*Fig. 33 Final outcome of solvolytically treated composite waste during this project period.*

The solvent can be re-used to degrade new supplies of composite materials. Furthermore, during the studies in this project, it has been found that the degradation products present in the solvent acts as additives and accelerate the degradation process. Re-using the solvent increases the sustainability of the process, due to savings of solvent and additives. After re-using the solvent for several runs, it can be distilled and re-used again.
The last products from the chemical solvolysis process are fuel oil and petro-chemicals. With a higher heating value up to 40 MJ/kg, the oil can be used either as a drop-in-fuel for refineries or used as the basis for potential chemical energy to run the process and make it energetically viable. In fact, with the results obtained from this PhD study, the oil produced in the process can potentially cover the energy requirements to degrade the composite and produce excess of energy at the same time. The goals set up in the beginning of the project can be considered fulfilled, cf. Fig. 34.

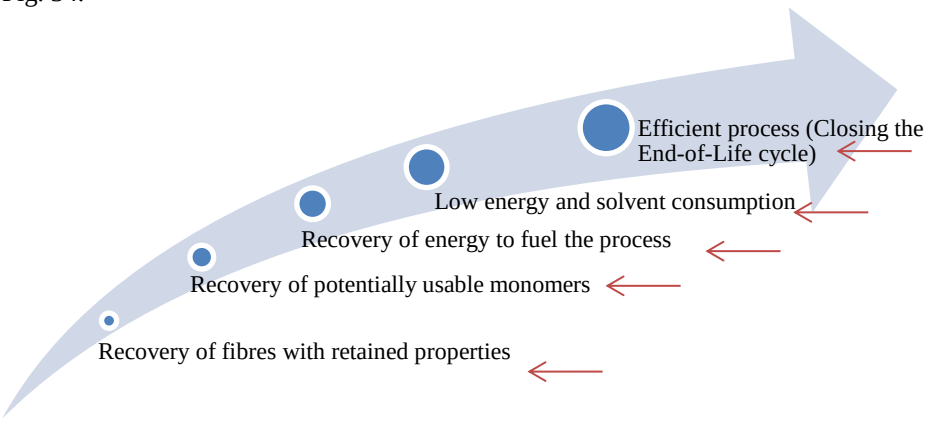


*Fig. 34 Fulfilled goals at the end of the project period.*

**General conclusion on composite waste management**
Although the findings in this study potentially can be useful to manage some of the composite waste problems, it is not considered as enough to tackle the polymer composite waste problem worldwide. The use of chemical recycling to recover the fibres with retained mechanical is possible. However, currently the process can only be conducted batch-wise. It is not possible, similarly as the production of bio-crude, to continuously pump feed into the reactor and get products out (fibres and solubilized resin). The "feed" (large composite specimens) is not pumpable. This means that the reactor has to be heated and cooled every time new supplies of composite waste have to be recycled, which is very expensive unit operations.
A suggestion that could be useful is to treat the composite waste from all the different industries with not only one technology, but with a mix of all the above mentioned technologies (mechanical recycling, thermal recycling and chemical recycling).

The selection of recycling technology will thus depend on the nature of the composite scrap (powdered, shredded, big parts etc.) and the desired end-products.

# Future perspectives

In the beginning of the PhD work, a period of 3 years seemed to be a long time to investigate the same field. I thought I would be able to cover all corners and edges during these years. However, sitting here at the final stage of the PhD, I know that a lot of investigations can be conducted in the future. Some of them include:

1. The glass- and carbon fibres recovered with retained mechanical properties in paper IV can be investigated further. This includes using them as reinforcement to produce a new composite material and then test the mechanical properties of the new composite. However, the time, materials and the equipment to conduct such research is not available.

2. Recovery of phthalic acid in paper VII can also be investigated further with respect to attaining higher quantities of the monomer. Extraction of highest possible amounts of the monomer will require longer reaction times inside the reactor (to depolymerize the matrix) at temperatures in the range of 275-300 °C. The monomer could then be extracted continuously or every 10-15 min. By storing the extracted liquid for several months, similarly as in paper VII, the phthalic acid monomer might crystallize and form solid fractions of purified phthalic acid, which can easily be separated from the remaining liquid and precipitate.

3. The production of petro-chemicals in paper IV is an interesting field with potential for further development. This includes distillation of the oil phase into fractions for example at 50-100 °C, 100-200°C, 200-300 °C and up to 600 °C. After analyzing the fractions, some of the chemicals in high quantity, e.g. 3,3,6,8-tetramethyl-1-tetralone, could potentially be separated and purified. The remaining part can be upgraded by help of catalysts and hydrogen.

4. Chemical recycling of composite waste could be conducted using a continuous reactor setup if the composite is powdered. During manufacturing of e.g. wind turbine blades, some of the production scrap is powdered composite, which can easily be turned into a pumpable slurry. Similarly as the process of converting biomass into biocrude, the powdered composite could continuously be converted into oil. The small fibres could hence be separated from the oil by centrifugation.

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# Appendix A Calculation of energy consumption

**Energy consumption to heat reactor vessel**

$m_{(\text{reactor of T316 stainless steel})}$ = 170.000 g

$\Delta T$ = 303 °C (22-325 °C) (Room temperature to operational temperature)

$Cp_{(\text{T316 stainless steel})}$ = 0.5 J/g °C (Data from MatWeb. The heat capacity of stainless
steel does not change significantly when temperature increase)

$E = 170.000\ g \cdot 303\ °C \cdot 0.5\ J/g\ °C = 2.58 \cdot 10^{7}\ J$

$1\ J = 2.778 \cdot 10^{-7}\ kWh$

$E = 2.778 \cdot 10^{-7}\ kWh \cdot 2.58 \cdot 10^{7}\ J$ = 7.16 kWh to heat up the reactor vessel

**Energy consumption to heat up 15 L water to 325 °C**

$m_{(water)}$ = 15.000 g

$\Delta T = T - T_{amb}$ (598.15 K – 295.15 K) = 303 K

$Cp_{(water)}$ = 5.5347 J/g K, at 325 °C and 300 bar (NIST)

$E = 15.000\ g \cdot 303\ K \cdot 5.5347\ J/g\ K = 2.5 \cdot 10^{7}\ J$

$E = 2.778 \cdot 10^{-7}\ kWh \cdot 2.5 \cdot 10^{7}\ J$ = 7 kWh to heat up 15.000 g water

**Total energy consumption to heat up solvent and reactor:** 7 kWh + 7.16 kWh = 14.16 kWh

**Conversion of calorific value to kWh**

Amount of oil = 2.7 kg

HHV at 325 °C = 40 MJ/kg

Chemical energy in 2.7 kg oil = 40 MJ/kg · 2.7 kg = 108 MJ

3.6 MJ corresponds to 1 kWh

Energy in kWh = 108 MJ/3.6 MJ = 30 kWh.

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